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SODIUM AND SILVER PHOSPHATE GLASSES DOPED WITH CHLORIDES OF Fe, Mn AND Zn

DSC study

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A number of samples of sodium and silver phosphate glasses doped with various compositions of some transition metals viz. iron, manganese and zinc chlorides alongwith undoped samples of sodium and silver phosphate glasses were synthesized and characterized by X-ray diffraction, IR spectral, electrical conductivity and differential scanning calorimetry (DSC). The glass transition temperature (T_g) and crystallization temperature (T_c) values obtained from DSC curves were found to increase with increasing concentration of the dopant Fe/Mn/Zn chlorides in both sodium and silver phosphate glasses and the following sequence is observed:

$$T_g(–FeCl_3)>T_g(–MnCl_2)>T_g(–ZnCl_2)$$

$$T_c(–FeCl_3)>T_c(–MnCl_2)>T_c(–ZnCl_2)$$

The increase in T_g and T_c values indicate enhanced chemical durability of the doped glasses. The electrical conductivity values and the results of FTIR spectral studies have been correlated with the structural changes in the glass matrix by the addition of different transition metal cations as dopants.

Keywords: *glass transition temperature, ion conduction glasses, iron phosphate glasses, silver phosphate glasses*

Introduction

Phosphate glasses are of potential interest because of ease of preparation at low temperatures, simple compositions, strong glass forming character, high ionic conductivities and diverse applications [1, 2]. However, their relatively poor chemical durability makes them generally unsuitable for practical applications [3]. The properties of the phosphate glasses can be modified and their chemical durability be increased by the addition of, generally, halides or oxides of the alkali, alkaline earth and transition metals into the glassy network [4]. Phosphate glasses doped with transition metals attract much attention because of their memorizing and photoconducting properties [5]. They also find potential application in solid-states batteries [6], solid-state lasers [7], luminescent solar energy concentrators (LCS) and optical fibres for communication devises [8–10]. The interest in sodium and silver phosphate glasses which contain transition metals got intensified as they have been shown to be promising glassy electrolytes for the development of technologically and biologically important materials [11–13].

The knowledge of thermal stability and phase transformation is essential for the understanding of molecular level structure, ion transport behaviour and several possible applications of these phosphate glasses. Due to this, thermal studies of such glasses have become important and DSC studies have successfully been used for the structural characterization of many phosphate glasses [14–19].

Thus, in the present paper we report the DSC studies of some newly synthesized sodium and silver phosphate glasses doped with Fe/Mn/Zn chlorides. The role of transition metal ions (Fe, Mn and Zn) in ascertaining T_g and T_c values were studied and compared. The results have been correlated with the IR spectral studies and electrical properties of these glasses.

Experimental

All the chemicals used in the preparation of glasses were of analytical grade. Sodium and silver phosphate glasses, both undoped and doped with Fe/Mn/Zn chloride, were prepared by employing the melt quenching technique [20]. For preparing transition metal chloride doped sodium and silver phosphate glasses, different amounts of Fe/Mn/$ZnCl_2$ were added to 1:1 molar mixture of Na_2CO_3:$NH_4H_2PO_4$ or $AgNO_3$:$NH_4H_2PO_4$, respectively. In each case of preparation two platinum crucibles were taken. In one platinum dish control sodium or silver phosphate glass were prepared and in the

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other metal chloride doped phosphate glasses were prepared. The mixtures were first heated slowly in an oven to 150–200°C and then in 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 and silver phosphate glasses were done on an automatic X-ray powder diffractometer.

IR spectral studies were carried out by using Perkin Elmer PC FTIR spectrometer in the range 4000–500 $\mathrm{cm^{-1}}$ using KBr pellets.

The electrical conductivities of all the glassy samples were measured with the help of Keithley 236 electrometer [21].

DSC studies were carried out by using STA 409 PC (Netzsch, Germany) instrument. In this study, the powder of the sample under investigation was taken in an aluminum pan with aluminum 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 $\mathrm{min^{-1}}$ under continuous nitrogen gas purging. The purging flow rate was kept constant at the rate of 20 mL $\mathrm{min^{-1}}$. DSC curves were recorded from room temperature to 450°C and the net heat flow was measured as a function of increasing temperature.

Results and discussion

X-ray diffraction patterns of all the samples show broad and diffused humps which indicate the amorphous nature of all the synthesized glasses. FTIR spectral analyses reveal the existence of symmetric bridging oxygen (P–O–P) and the presence of two non-bridging oxygen atoms ($\mathrm{P{-}O^{-}}$) in the phosphate tertahedra [22] of all the glassy systems.

The values of T_g and T_c for all the sodium and silver phosphate glasses doped with chlorides of Fe/Mn/Zn as determined from DSC curves are given in Table 1. The results show that the T_g values of the undoped sodium and silver phosphate glasses are 286.1 and 194.6°C, respectively. It is observed that the T_g and T_c values are found to increase with the increase in dopant (Fe/Mn/$\mathrm{ZnCl_2}$) concentrations in case of both sodium and silver phosphate glasses. The T_g values increase from 292.4 to 326.1°C in $\mathrm{Na_2O{-}P_2O_5{-}FeCl_3}$; from 290.1 to 316.2°C in $\mathrm{Na_2O{-}P_2O_5{-}MnCl_2}$; from 287.7 to 307.5°C in $\mathrm{Na_2O{-}P_2O_5{-}ZnCl_2}$; from 208.8 to 232.9°C in $\mathrm{Ag_2O{-}P_2O_5{-}FeCl_3}$; from 203.1 to 221.6°C in $\mathrm{Ag_2O{-}P_2O_5{-}MnCl_2}$ and from 197.3 to 208.2°C in $\mathrm{Ag_2O{-}P_2O_5{-}ZnCl_2}$ glassy systems when the dopant ($\mathrm{FeCl_3/MnCl_2/ZnCl_2}$) concentrations were increased from 1 to 10%. Similar increasing behaviour for T_c values (Table 1) were also found in all the glasses and the following sequence in T_g and T_c values are observed:

$$T_g(\mathrm{-FeCl_3})>T_g(\mathrm{-MnCl_2})>T_g(\mathrm{-ZnCl_2})$$

and

$$T_c(\mathrm{-FeCl_3})>T_c(\mathrm{-MnCl_2})>T_c(\mathrm{-ZnCl_2})$$

The network of phosphate glass consists of Q^3 type $\mathrm{PO_4}$ tetrahedra where three of the oxygens are bridging (P–O–P) and one is non-bridging (P=O), as shown in Fig. 1. When alkali oxide $\mathrm{Na_2O}$ (or $\mathrm{Ag_2O}$) is added into the $\mathrm{PO_4}$ network of phosphate glass, it converts three dimensional network into linear phosphate chains [23] with the cleavage of P–O–P linkages and creation of non-bridging oxygen atoms in the glass which has an intrinsic polymeric feature [24]. P–O–P bridging oxygens are converted to $\mathrm{P{-}O^{-}{-}M^{+}}$ non-bridging oxygens (where $M^{+}=\mathrm{Na^{+}}$ or $\mathrm{Ag^{+}}$), which indicates the formation of Q^2 tetrahedra (Fig. 1) with two bridging and two non-bridging oxygen atoms [25] and the two non-bridging oxygen bonds are in resonance with each other [26].

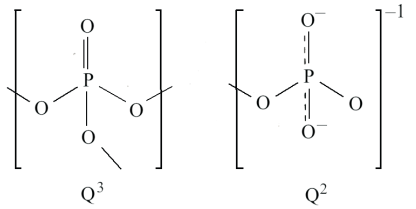

Fig. 1 The Q^3 and Q^2 tetrahedral units in phosphate glasses

The structure of undoped sodium/silver phosphate glass with the formation of $\mathrm{P}\overset{\cdots}{=}\mathrm{O^{-}}\cdots\mathrm{M^{+}}$ (where $M^{+}=\mathrm{Na^{+}/Ag^{+}}$) bond [27] is shown in Fig. 2a. When $\mathrm{MnCl_2}$ or $\mathrm{ZnCl_2}$ are added in the undoped glass formation of P–O–M bonds (where $M=\mathrm{Mn^{2+}}$ or $\mathrm{Zn^{2+}}$) occur in the glass structure which replaces the $\mathrm{P}\overset{\cdots}{=}\mathrm{O^{-}}\cdots\mathrm{M^{+}}$ bonds [28]. The structure of Mn/$\mathrm{ZnCl_2}$ doped glasses can be considered to possess Q^2 type chains where the dopant cations $\mathrm{Mn^{2+}/Zn^{2+}}$ can be considered to serve as ionic cross-links between the non-bridging oxygen of two different phosphate chains of sodium/silver phosphate glasses as shown in Fig. 2b. The cross-linking of phosphate chains would result in an increase in the strength of the glass network structure. With increasing concentrations of the dopant chlorides, the number of ionic cross-links increases which eventually lead to an increase in T_g

Table 1 Glass transition temperature (T_g), crystallization temperature (T_c) and conductivity values of various sodium and silver phosphate glasses

S. No.	Phosphate glasses	Glass transition temperature, T_g/°C	Crystallization temperature, T_c/°C	Conductivity, σ/S cm^{-1}	
				at room temperature	at 150°C
1	$Na_2O–P_2O_5$	286.1	359.0	$3.13\cdot10^{-9}$	$1.52\cdot10^{-6}$
2	$Na_2O–P_2O_5$–1% $FeCl_3$	292.4	363.5	$1.32\cdot10^{-8}$	$2.50\cdot10^{-6}$
3	$Na_2O–P_2O_5$–2.5% $FeCl_3$	299.8	365.1	$9.52\cdot10^{-9}$	
4	$Na_2O–P_2O_5$–5% $FeCl_3$	306.1	368.6	$9.19\cdot10^{-9}$	
5	$Na_2O–P_2O_5$–7.5% $FeCl_3$	313.5	374.7	$6.17\cdot10^{-9}$	
6	$Na_2O–P_2O_5$–10% $FeCl_3$	326.1	380.2	$1.15\cdot10^{-9}$	
7	$Na_2O–P_2O_5$–1% $MnCl_2$	290.1	360.4	$8.22\cdot10^{-9}$	
8	$Na_2O–P_2O_5$–2.5% $MnCl_2$	297.9	364.1	$9.62\cdot10^{-9}$	
9	$Na_2O–P_2O_5$–5% $MnCl_2$	304.0	371.8	$1.63\cdot10^{-8}$	$4.23\cdot10^{-6}$
10	$Na_2O–P_2O_5$–7.5% $MnCl_2$	309.4	373.2	$1.44\cdot10^{-8}$	
11	$Na_2O–P_2O_5$–10% $MnCl_2$	316.2	376.3	$1.15\cdot10^{-8}$	
12	$Na_2O–P_2O_5$–1% $ZnCl_2$	287.7	355.5	$3.37\cdot10^{-8}$	
13	$Na_2O–P_2O_5$–2.5% $ZnCl_2$	294.6	359.1	$4.45\cdot10^{-8}$	
14	$Na_2O–P_2O_5$–5% $ZnCl_2$	299.6	363.3	$6.59\cdot10^{-8}$	$3.16\cdot10^{-5}$
15	$Na_2O–P_2O_5$–7.5% $ZnCl_2$	303.4	366.8	$4.56\cdot10^{-8}$	
16	$Na_2O–P_2O_5$–10% $ZnCl_2$	307.5	372.8	$2.42\cdot10^{-8}$	
17	$Ag_2O–P_2O_5$	194.5	316.8	$1.95\cdot10^{-7}$	$1.28\cdot10^{-5}$
18	$Ag_2O–P_2O_5$–1% $FeCl_3$	208.8	329.2	$5.24\cdot10^{-7}$	$4.53\cdot10^{-5}$
19	$Ag_2O–P_2O_5$–2.5% $FeCl_3$	214.1	333.5	$4.12\cdot10^{-7}$	
20	$Ag_2O–P_2O_5$–5% $FeCl_3$	224.6	338.8	$2.03\cdot10^{-7}$	
21	$Ag_2O–P_2O_5$–7.5% $FeCl_3$	228.5	343.1	$1.92\cdot10^{-7}$	
22	$Ag_2O–P_2O_5$–10% $FeCl_3$	232.9	349.2	$4.25\cdot10^{-8}$	
23	$Ag_2O–P_2O_5$–1% $MnCl_2$	203.1	322.2	$2.14\cdot10^{-7}$	
24	$Ag_2O–P_2O_5$–2.5% $MnCl_2$	207.7	327.9	$4.29\cdot10^{-7}$	
25	$Ag_2O–P_2O_5$–5% $MnCl_2$	212.4	332.8	$5.34\cdot10^{-7}$	$8.48\cdot10^{-5}$
26	$Ag_2O–P_2O_5$–7.5% $MnCl_2$	216.5	336.1	$3.20\cdot10^{-7}$	
27	$Ag_2O–P_2O_5$–10% $MnCl_2$	221.6	340.4	$2.17\cdot10^{-7}$	
28	$Ag_2O–P_2O_5$–1% $ZnCl_2$	197.3	318.1	$9.23\cdot10^{-6}$	
29	$Ag_2O–P_2O_5$–2.5% $ZnCl_2$	198.6	321.4	$2.23\cdot10^{-5}$	
30	$Ag_2O–P_2O_5$–5% $ZnCl_2$	201.1	326.8	$4.13\cdot10^{-5}$	
31	$Ag_2O–P_2O_5$–7.5% $ZnCl_2$	204.9	330.2	$5.46\cdot10^{-5}$	
32	$Ag_2O–P_2O_5$–10% $ZnCl_2$	208.2	335.3	$6.65\cdot10^{-5}$	$1.10\cdot10^{-4}$

and T_c values of all the synthesized glasses [29]. The higher T_g values of $MnCl_2$ doped glasses in comparison to $ZnCl_2$ doped ones could be explained on the basis of ion size [30] of cations although both the ions (Mn^{2+} and Zn^{2+}) have octahedral coordination sites [31, 32]. Mn^{2+} ions being smaller in size will lead to close packed structure while the bigger Zn^{2+} ion would form loosened glassy structure and hence the T_g values of the closed packed glassy systems are found to be higher than the loosened ones. The mobility of cations (Na^+ or Ag^+) in $MnCl_2$ doped glasses will have lesser values due to closed packed structure, as such the conductivity values of $MnCl_2$ doped sodium/silver phosphate glasses should be lower than the loosely packed $ZnCl_2$ doped ones. The higher σ values (Table 1) in all the $ZnCl_2$ doped glassy systems supports the above explanations.

However, when $FeCl_3$ is used as dopant then formation of P–O–M bonds (where M=Fe^{3+}) in the glass structure would probably occur where Fe^{3+} ions presumed to serves as ionic cross-links between three non-bridging oxygen of three different phosphate chains of sodium/silver phosphate glasses (Fig. 2c).

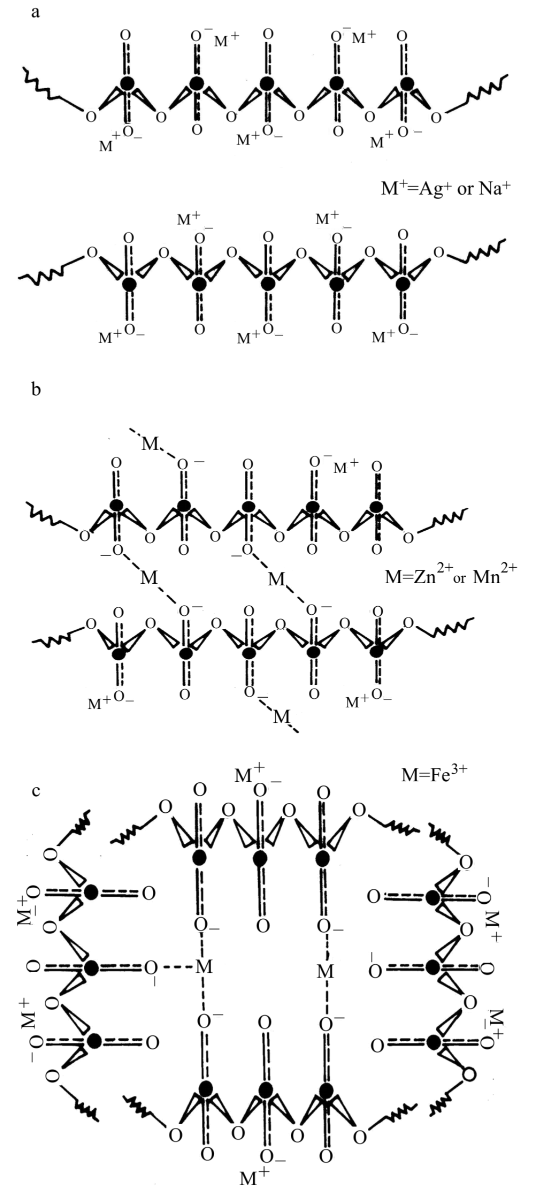

Fig. 2a–c Schematic structures of a – undoped b – $MnCl_2$ or $ZnCl_2$ doped and c – $FeCl_3$ doped sodium or silver phosphate glasses

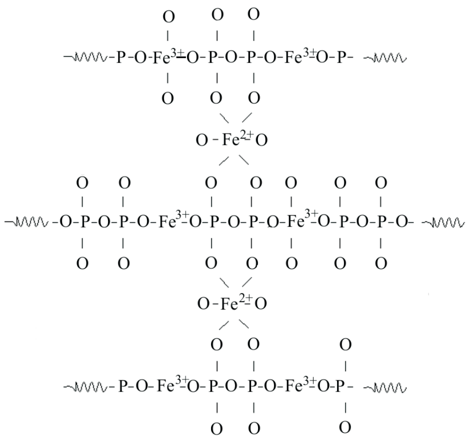

Fig. 2d Proposed structure [12] for iron chloride doped sodium or silver phosphate glass where iron(II) ions are in octahedral sites and iron(III) ions in tetrahedral coordination. The Na^+ or Ag^+ ions are not shown in this figure for the sake of simplicity

But in $FeCl_3$ doped glasses presence of both Fe(II) and Fe(III) states are expected to play different structural roles [33]. The P–O–M bonds are believed to be replaced either by P–O–Fe(III) or P–O–Fe(II) bonds. It has been reported that in iron phosphate glasses Fe(II) ions are in octahedral coordination, whereas, Fe(III) ions have octahedral or distorted octahedral coordinations [12, 34]. On this basis, the most plausible structure of $FeCl_3$ doped sodium/silver phosphate glasses have been proposed in Fig. 2d in which strong cross-linking of the phosphate chains by Fe^{2+} ions exists. Thus, the cross-link density of $FeCl_3$ doped sodium/silver phosphate glasses will be much more as compared to $Mn/ZnCl_2$ doped ones. Consequently the T_g and T_c values in $FeCl_3$ doped glassy systems should be maximum. The higher T_g and T_c values of all the synthesized $FeCl_3$ doped phosphate glasses (Table 1) in comparison to $Mn/ZnCl_2$ doped ones supports this argument. The low σ values in all the $FeCl_3$ doped sodium/silver phosphate glasses (Table 1) further support strong cross-linking of the chains in these glasses which reduces the mobility of the cations (Na^+ or Ag^+) due to more closely packed glassy matrix.

Further, it is also observed that T_g and T_c values are high in the case of all the sodium phosphate glasses. The higher values of T_g and T_c of undoped and the doped sodium phosphate glasses in comparison to the silver phosphate glassy systems could be explained on the basis of ion size of Na^+ and Ag^+. The Ag^+ ions with larger ion size [30] will eventually form loosened glassy network, and hence possess lower T_g and T_c values. The more loosened glassy network would enhance the mobility of free Ag^+ ions and hence the conductivity will increase. The higher σ values in all the synthesized silver phosphate glasses in comparison to sodium phosphate ones supports the above explanation.

Conclusions

Addition of iron/manganese/zinc chlorides in sodium/silver phosphate glasses increase the T_g and T_c values. These values increase when the concentration of the dopant $Fe/Mn/ZnCl_2$ increases. This has been explained on the basis of increase in the strength of glass network structure due to cross-linking of the phosphate chains. The increase in T_g and T_c values indicate enhanced chemical durability of the doped glasses and it is found that $FeCl_3$ doped sodium and silver phosphate glasses have the maximum chemical durability. However, the T_g and T_c values of sodium phosphate glasses are higher than those of silver phosphate glasses. The electrical conductivity values are in accordance with the structural changes in the glass matrix caused by the addition of different metal cations as dopants.

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References

1 R. K Brow, J. Non-Cryst. Solids, 263 (2000) 1.
2 M. D. Ingram, Curr. Opin. Solid State Mater. Sci., 2 (1997) 399.
3 H. Yung, P. Y. Shih, H. S. Liu and T. S. Chin, J. Am. Ceram. Soc., 80 (1997) 2213.
4 R. K. Brow, J. Am. Ceram. Soc., 76 (1993) 913.
5 G. R. Moridi and C. A. Horgarth, Int. J. Electron, 44 (1978) 297.
6 S. S. Das, B. P. Baranwal , C. P. Gupta and P. Singh, J. Power Sources, 114 (2003) 346.
7 L. E. Bausa, F. Jaque, J. G. Sole and A. Duran, J. Mater. Sci., 23 (1998) 1921.
8 M. Jamnicky, P. Znasik, D. Tunega and M. D. Ingram, J. Non-Cryst. Solids, 185 (1995) 151.
9 U. Selveraj and K. J. Rao, J. Non-Cryst. Solids, 72 (1985) 315.
10 S. H. Kim and T. Yoko, J. Am. Ceram. Soc., 78 (1995) 1061.
11 C. Hunter and M. D. Ingram, Phys. Chem. Glasses, 27 (1986) 51.
12 X. Yu, D. E. Day, G. J. Long and R. K. Brow, J. Non-Cryst. Solids, 215 (1997) 21.
13 L. Murawski, R. J. Barczynski and D. Samatowicz, J. Solid State Ionics, 157 (2003) 293.
14 A. A. Kutub and A. S. Shawoosh, J. Mater. Sci., 32 (1997) 5491.
15 P. Y. Shih, S. W. Yung and T. S. Chin, J. Non-Cryst. Solids, 224 (1998) 143.
16 S. S. Das, B. P. Barnwal, C. P. Gupta and P. Singh, Indian J. Eng. Mater. Sci., 12 (2005) 58.
17 S. S. Das and P. Chin, J. Therm. Anal. Cal., 78 (2004) 731.
18 D. V. Bavbande, R. Misra and J. M. Juneja, J. Therm. Anal. Cal., 78 (2004) 775.
19 Zs. Éhen, F. Giordano, L. Jicsinszky, J. Sztatisz and Cs. Novák, J .Therm. Anal. Cal., 80 (2005) 419.
20 S. S. Das, B. P. Barnwal, S. A. Rayeeny and C. P. Gupta, Phys. Chem. Glasses, 42 (2001) 74.
21 A. Mogus-Milankovic, B. Santic, D. E. Day and C. S. Ray, J. Non-Cryst. Solids, 283 (2001) 119.
22 K. Meyer, J. Non-Cryst. Solids, 209 (1997) 227.
23 Y. M. Moustafa and K. El- Egili, J. Non-Cryst. Solids, 240 (1998) 144.
24 S. W. Martin, Eur. J. Solid State Inorg. Chem., 28 (1991) 163.
25 D. L. Sidebottom, Phys. Rev. B, 61 (2000) 14507.
26 R. Gresch, W. Muller-Warmuth and H. Dutz, J. Non-Cryst. Solids, 34 (1979) 127.
27 P. Y. Shih, S. W. Yung and T. S. Chin, J. Non-Cryst. Solids, 244 (1999) 211.
28 S. A. Agnihotry, S. S. Das and P. Singh, J. Non-Cryst. Solids, 351 (2005) 3730.
29 P. Y. Shih, Mater. Chem. Phys., 84 (2004) 151.
30 J. D. Lee, Concise Inorganic Chemistry, (5th Edn), Black Well Science, USAC, (1999).
31 L. Montagne, G. Palavit and R. Delaval, J. Non-Cryst. Solids, 215 (1997) 1.
32 I. Bratu, I. Ardelean, A. Barbu, V. Mih, D. Maniu and G. Botezan, J. Mol. Structure, 482–483 (1999) 689.
33 G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, M. G. Shumsky, W. B. Yelon, C. H. Booth, P. G. Allen and D. K. Shuh, J. Non-Cryst. Solids, 222 (1997) 144.
34 B. Pivac, A. Mogus-Milankovic and D. E. Day, J. Non-Cryst. Solids, 226 (1998) 41.

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