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Properties of oxychloride glass system in relation to fast ion conduction

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Abstract. A series of glasses based on the $0.2\text{MoO}_3\text{-}0.3\text{P}_2\text{O}_5\text{-(}0.5-x\text{)PbO-xPbCl}_2$ system was prepared and their physical and thermal properties were investigated. This system provides a wide and stable glass formation range in which improvement of ionic conductivity would be achieved. The composition dependence of some properties was discussed in terms of the possible role of chlorine ions in the glass structure. The experimental data suggested that Cl^- ion accommodation could form additional preferential pathways which are important for the conduction mechanism. The glass corresponding to composition $x = 0.45$ was found to have the highest conductivity value ($\sim 10^{-2} \text{ S cm}^{-1}$) which recommends it for possible technological applications.

1. Introduction

The phenomenon of fast ion conduction in both binary and ternary glasses has been extensively studied [1–9]. Greater efforts have now been directed towards the study of the phenomenon in more complicated systems which may be called ‘mixed former’ or quaternary systems [10–15]. The glasses in the latter systems have advantages over both binary and ternary glasses; this may be for the following reasons: the quaternary glasses contain at least two glass formers and the simultaneous use of these networks improves the conductivity by some orders of magnitude in comparison to those of individual glasses [3, 16–18]. Moreover, in binary and ternary systems, the glass formation is limited to a certain amount of doping salt while the quaternary glasses are characterized by a wide range of property control. Thus the ease of forming glasses with different compositions and isotropic properties has led to a new interest in the study of quaternary glass systems [10–12].

Recently we have carried out a significant number of studies on glasses containing different metal halides (PbX , AgX , $\text{X} = \text{Cl, Br}$) [1, 3, 10, 11]. These studies have shown that these glasses can be formed over a wide composition range. Also most of the previous works [10–15, 18] on the quaternary system have been focused on the characterization of the quaternary superionic glasses containing silver and/or alkali halides as dopant materials.

Study of PbCl_2 in quaternary glasses has been much more limited, to the best of my knowledge [10], since there is no publication available on quaternary $\text{PbCl}_2\text{-PbO-MoO}_3\text{-P}_2\text{O}_5$ glasses. Therefore, the present work is devoted to reporting the behaviour and properties of quaternary lead oxychloride glasses based on the $\text{MoO}_3\text{-P}_2\text{O}_5$ system (halogenated lead molybdophosphate). It also aims to obtain physical insight into the nature of charge motion and to study the influence of chlorine ions on the conduction mechanism.

2. Experimental procedures

2.1. Glass preparation

Glasses were prepared from the starting materials, reagent grade PbO, PbCl₂, MoO₃ and NH₄H₂PO₄. The composition of the glasses is based on the progressive replacement of PbO by PbCl₂ while holding MoO₃ and P₂O₅ concentrations constant.

Glass syntheses were carried out by mixing appropriate amounts of the above mentioned chemicals. They are prepared by the direct melting process, where the mixture (except PbCl₂) was heated in a covered platinum crucible in an electric furnace, first at 180 and 400 °C for one hour to minimize material volatilization. The product was then melted between 700 and 900 °C for 30 minutes, depending on its composition, with periodic swirling to ensure homogeneity and the attainment of thermal and chemical equilibrium. Then, PbCl₂ was added to the melt and the melting process continued for a short time (15 minutes) in a covered crucible to minimize probable chlorine or phosphorus losses. After refining, the melt was poured by pressing the sample between two stainless steel plates to yield disc shaped samples. The probable Cl⁻ losses were estimated to be 0.3–0.5 mol%. All samples prepared were analysed by x-ray diffraction to confirm non-crystallinity.

2.2. Property measurements

Glass transformation temperature T_g was determined using a Shimadzu (DTA-50) thermal analyser with a heating rate of 10 K min⁻¹. The reproducibility in T_g was ±2 K. Measurements of the thermal expansion coefficient (α) were carried out using a dial gauge with 0.01 mm sensitivity [11]. The temperature of the glass sample was controlled by an NiCr–Ni thermocouple close to the sample surface. A sample 30–40 mm long was heated at 5 K min⁻¹ to slightly above the softening temperature. The average thermal expansion coefficients were determined over the temperature range, which is below T_g in all glass samples. Glass transition temperatures (±3 K) were also determined from the thermal expansion curves using the slope–intercept method [19]. The accuracy of the measured value of α was found to be within ±2%.

For microhardness measurements H_v , the surfaces of the glassy sample were finely polished before measurement. The indenter was set using a uniform load of 50 g and then penetrated slowly into the glass for a constant indenter dwell time of 10 s. At least ten indentations were taken in different locations on each specimen. Microhardness number H_v was obtained using an FM7 microhardness tester (Japan). The reproducibility of H_v for two samples of each composition was about ±5 kg mm⁻².

The density of the glassy samples (295 K) was determined by measuring their apparent loss of weight in xylene (density = 0.865 g cm⁻³) using an electronic balance with sensitivity of 10⁻⁴ g. The densities were accurate to ±0.01 g cm⁻³. Molar volumes were calculated from the known molecular weights.

Ac electrical conductivity of the glass sample was measured as a function of temperature (30–150 °C) using an impedance meter (type Tesla BM 507). The flat surfaces of the studied samples were silver coated. The frequency range of the measurement was extended from 5 Hz up to 20 kHz. The dc conductivity data for all the glass compositions are extracted from the conventional complex impedance analysis [11, 20]. To insure reliable and reproducible conductivity data, careful attention was paid to the conductance cell. The two terminal electrodes were made from silver and electrically shielded. The temperature of the glassy sample was monitored using an NiCr–Ni thermocouple attached to the sample.

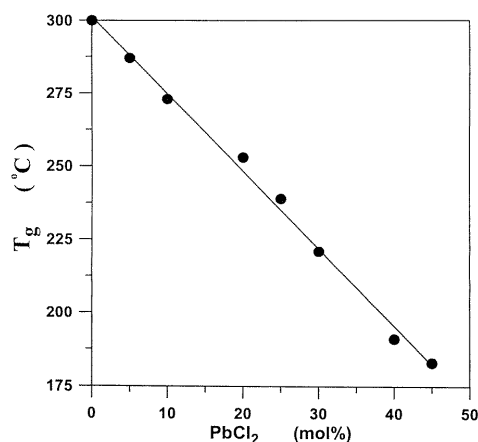


Figure 1. Variation in glass transition temperature with composition of $x\text{PbCl}_2-(0.5-x)\text{PbO}-0.2\text{MoO}_3-0.3\text{P}_2\text{O}_5$ glasses.

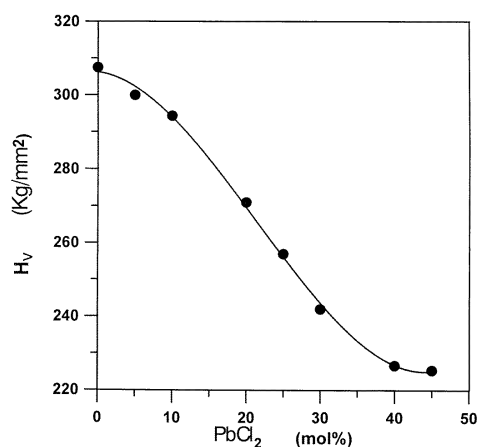


Figure 2. Effect of glass composition on the microhardness numbers, H_v for the $\text{PbCl}_2\text{-PbO-MoO}_3\text{-P}_2\text{O}_5$ glass system.

3. Results

The effect of glass composition on the glass transformation, T_g of the glasses studied in the system $x\text{PbCl}_2-(0.5-x)\text{PbO}-0.2\text{MoO}_3-0.3\text{P}_2\text{O}_5$ is shown in figure 1. The value of T_g decreases gradually with increasing PbCl_2 concentration, indicating that the disruption of the network by chlorine ions dominates the value of T_g at high PbCl_2 content. The microhardness number, H_v of these glasses is presented in figure 2. It may be noticed that the microhardness values decrease continuously with the gradual replacement of PbO by PbCl_2 . Therefore, this suggests that deformation of the covalently bonded structure is expected to be present in those glass compositions. The average thermal expansion α (figure 3) increases monotonically by a factor of about three as PbCl_2 replaces PbO in the glass composition. The thermal expansion coefficients are found to have higher values than those of the previously studied $\text{PbCl}_2\text{-PbO-MoO}_3\text{-B}_2\text{O}_3$ system [10]. Variation of molar volumes as a function of substitution of PbO

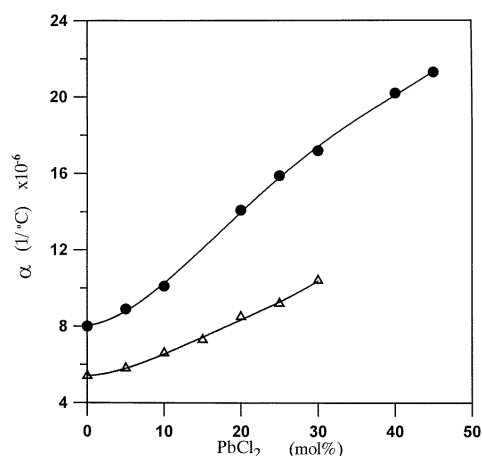


Figure 3. Dependence upon composition of the thermal expansion coefficients of the present work (closed circles) and the $\text{PbCl}_2\text{-PbO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glass system (open triangles) [10].

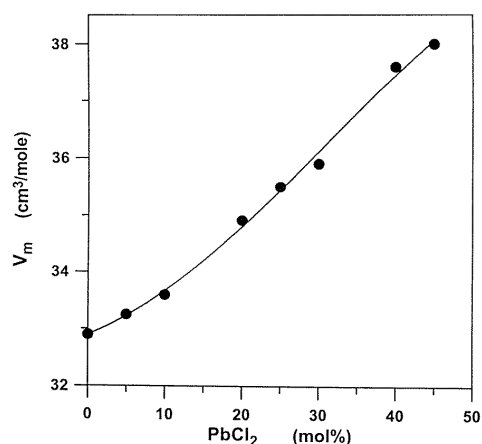


Figure 4. Variation of molar volume for $\text{PbCl}_2\text{-PbO-MoO}_3\text{-P}_2\text{O}_5$ as a function of PbCl_2 concentration.

by PbCl_2 for the studied glasses is plotted in figure 4. It is interesting to note that the molar volume increases as PbCl_2 replaces PbO .

Figure 5 shows the dependence of ionic conductivity σ (at 373 K) and the associated activation energy for conduction on glass composition. It is observed that the conductivity increases over five orders of magnitude with increasing PbCl_2 content and reaches a maximum value for $x = 0.45$, while the activation energy decreases. The experimental error in determining the activation energy for conduction is estimated to be less than 0.02 eV, whereas the relative error of conductivity is about $\pm 5\%$. A comparison between conductivities of the present glass system (filled circles) and those of previously reported observations [10] (open triangles) is represented in figure 6 as the amount of PbCl_2 increases. A higher conduction is observed than previously.

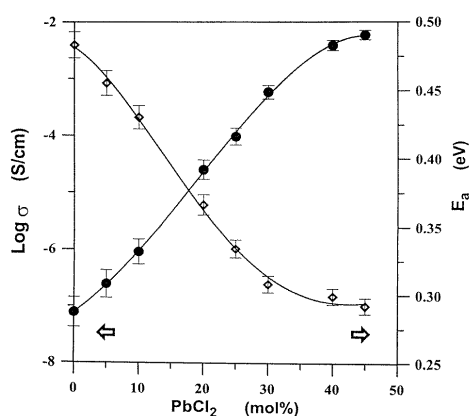


Figure 5. Composition dependence of conductivity at 373 K and the activation energy for conduction for glasses in the present system.

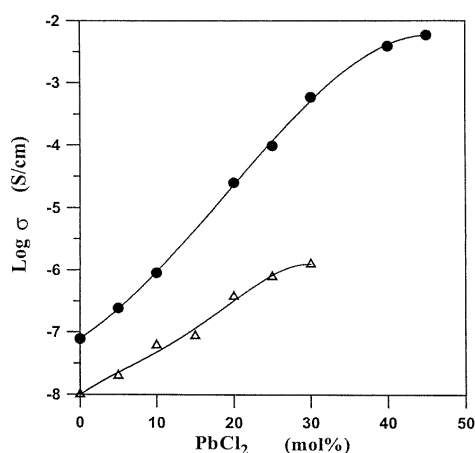


Figure 6. Comparison of the electrical conductivity of PbCl₂-PbO-MoO₃-P₂O₅ glasses (closed circles) with that reported [10] for PbCl₂-PbO-B₂O₃-P₂O₅ glasses (open triangles).

4. Discussion

Before attempting to interpret the results obtained in the present investigation, a brief summary of the structural information on P₂O₅ and MoO₃ as well as structural modification with network modifier is important to consider. This is imperative for further elucidating the understanding of the quaternary glass properties.

It is well known [21, 22] that the glassy P₂O₅ consists of PO₄ units with one double bonded oxygen and three bridging oxygen atoms. When a small amount of modifier, i.e. M₂O (M = Ag, Li, Na etc) is added, a change in the PO₄ unit takes place. The modifier creates a negative charge on one of the bridging oxygens. This situation ends at the meta-phosphate composition (MPO₃). Further addition of the modifier causes the formation of monomeric units, M₄P₂O₇, M₃PO₄, ... etc.

In molybdenum trioxide, MoO₃, the M-O bond may be considered covalent [23]. The MoO₃ provides octahedral units [MoO_{6/2}] that are necessary for the extensive network formation.

MoO₃ and P₂O₅ form stable glasses over a wide range of composition [24]. In the absence of an alkali oxide component, the molybdenum phosphate glasses are presumably composed of joined [MoO_{6/2}] octahedra and [POO_{3/2}] tetrahedra sharing oxygen corners [25, 26]. The structure of such oxide glasses, characterized by the presence of extensive two- and three-dimensional networks, is modified by the addition of some metal oxides. As a result of such modification, network terminations of the type Mo–O[−] and P–O[−] are formed. Addition of enough modifier oxide results in formation of discrete phosphate and molybdate anions in the glass. The coordination number of molybdenum may decrease to four by the formation of MoO₄ units. The resulting M₂O–MoO₃–P₂O₅ glasses [25, 27] may contain mixed polyhedra and a truncated network.

When PbO is introduced into the molybdophosphate network, as in the present investigation, it may play a dual structural role, partly the role of a glass forming oxide in the form of PbO₄ pyramidal units which are incorporated into the structure in corner sharing geometry. The additional oxygens needed for the coordination of Pb can be provided by the [POO_{3/2}] units in the host network [28]. On the other hand, PbO can be incorporated into the network as a modifier. Pb²⁺ ions however are located in the structure as interstitial ions with large coordination and break the various linkages resulting in the formation of different structural units.

It is worth noting that introduction of halide ions into a glass is accompanied by changes in the glass properties. In the system under study, the strong covalent P–O and Mo–O bonds in the glassy network probably replaced by apparently weaker ionic bonds of the Pb²⁺–O^{2−} type. As may be seen in figure 1, increasing PbCl₂ content strongly affects the transformation temperature T_g of the glasses studied. T_g decreases gradually with the replacement of PbO by PbCl₂. However, the change in T_g would generally be attributed to the combined effect of the change in bond strength, degree of cross-link density and closeness of packing [11, 29]. Therefore, the observed decrease in T_g should be correlated with breaking of the network, contributing to its loosening and consequently decreasing the bond strength. Moreover, a more weakened structure is expected to be formed. Obviously, the latter observation is consistent with the decrease in hardness number H_v , shown in figure 2.

The hardness of the glass is often equated with its resistance to abrasion since it may determine the durability of the glass during use and it may also decide the suitability of the glass for special applications. Several authors have investigated the relationship between microhardness and softening [11, 30, 31] of glasses to support the idea that H_v can be considered as a property typical of glass strength. Therefore, the bond weakening alkali cation of the present glasses is assumed to be responsible for the observed softening and consequently the observed decrease in microhardness as the amount of PbCl₂ increases. The continuous decrease of H_v for the glasses studied reveals that the fragility nature of the network may be increased (i.e. a weaker structure obtained).

It has been suggested [32] that the bond strength and the nature of the bond govern the thermal expansion (α). An open, less rigid or loose structure favours an increase in α . Therefore, the increase of α with increasing PbCl₂ content, figure 3, can be ascribed to the elongation or rupture of some bonds such as P–O–P, Mo–O–Mo and/or P–O–Mo in addition to Pb–O–P linkages due to accommodation of chlorine ions. Moreover, the binding energy decreases with decreasing valency and increasing size of the added atoms (Cl[−] ions) [33, 34]. Consequently, as the amount of ionic bonding increases, the thermal expansion coefficient is also assumed to increase, the expanded network of the current system being in a good agreement with those reported for increasing inter-ionic separation and decreasing oxygen packing density [11, 15]. In comparison to a previously reported observation [10], the thermal expansion coefficients of the present quaternary oxychloride based on the Mo₃–P₂O₅ system,

however, increase much more rapidly with the increase of PbCl_2 content than do those of lead halogenated borophosphate glasses [10]. This observation would be interpreted as substitution of PbCl_2 for PbO in $\text{MoO}_3\text{-P}_2\text{O}_5$ further weakening the covalently bonded structure to a greater extent than in $\text{B}_2\text{O}_3\text{-P}_2\text{O}_5$.

The arguments presented above lead one to conclude that the thermal expansion increases and both the transformation temperature and hardness number decrease on the replacement of one O^{2-} ion by another larger two Cl^- ions (lower field strength). In agreement with results reported by Uhlman and Shaw [35], the larger the size of the ion, the greater is its effect on increasing the thermal expansion coefficient and on decreasing both the transformation and the softening temperatures.

On the basis of the above discussion, the correlation of fragility with thermal properties of the present glass system seems to be straightforward if one looks at fragility as decreasing of both T_g and H_v and increasing of α in contrast to normal glasses [36].

Evidence for the expanded network structure upon addition of chlorine ions can be obtained from the change of molar volume, see figure 4. It can be observed from this figure that increasing PbCl_2 content leads to extra increase of molar volume. This was expected, since two Cl^- ions (ionic radius = 1.83 Å) are replacing one O^{2-} ion (ionic radius = 1.32 Å). Chlorine ions are considerably heavier than oxygen ions beside the larger ionic size. Therefore, the increase in the molar volume of the glasses studied as chlorine replaces oxygen clearly demonstrates the effect of chlorine in increasing the volume of the structure. This leads one to conclude that the increase of molar volume (figure 4) with increasing PbCl_2 content supports the present results of the thermal expansion, indicating some correlations, that the structure is more opened and expanded with PbCl_2 accommodation.

The change in the above physical properties, e.g. T_g , H_v , α and V_m with composition may give some information about the nature of the glass network. So measurements of these properties would be able to reveal the electrical behaviour of the glasses studied. The electrical conductivity σ of the $x\text{PbCl}_2\text{-(}0.5 - x\text{)PbO-}0.2\text{MoO}_3\text{-}0.3\text{P}_2\text{O}_5$ system is shown to be improved with further increases of PbCl_2 content, reaching a maximum value at $x = 0.45$. The dependence of ionic conductivity on PbCl_2 content is represented in figure 5. It is observed that the conductivity increases even with the initial substitution of PbCl_2 for PbO and is almost five orders of magnitude. The observed enhancement in conductivity may indicate that the concentration of mobile ions increases when replacing PbO by PbCl_2 . This leads one to suggest that Pb^{2+} ion associated with Cl^- is more mobile than that associated with O^{2-} . Therefore, the conductivity enhancement would then be caused by changes in the mobility of Pb^{2+} ions. This suggestion is in good agreement with that previously reported by several authors [1, 3, 10, 37–39] on different glass systems containing PbX_2 ($X = \text{Cl, Br, I}$). They argued that the conduction is mainly cationic by Pb^{2+} as charge-carrying species, while the addition of halogen enhanced the conductivity through creating pathways between loosely packed Cl^- ions. Studies of lead chlorosilicate glasses [40] postulated that there are some consequences of anionic conduction by Cl^- ions.

Correlating the arguments presented above with the obtained results of the present glasses gives evidence to deduce that the type of charge-carrying species depends essentially on the concentration of the halide salt and on the overall glass composition. Consequently, one would conclude that Pb^{2+} ion is the major charge-carrying species. In other words, a limited number of Cl^- ions may contribute to the conductivity, particularly in glasses containing a higher amount of PbCl_2 (>40 mol%) [41].

Another factor affecting the conduction behaviour of the present glasses is the size of chlorine ion (discussed above) which is quite large (1.81 Å). Addition of Cl^- ions instead of oxygen causes a destruction in the network due to the accommodation of the excess chlorine

ions. Accordingly, this leads one to deduce that the role of chlorine ion in the conduction process can be understood by considering the formation of more open spaces in the network, which is favourable for charge carrier diffusion, resulting in increasing mobility of Pb^{2+} ions. In this regard, the weakened nature of the lead molybdophosphate network as a result of the presence of Cl^- ions is also accounted for by the increasing mobility of Pb^{2+} ions and consequently improves the electrical conductivity.

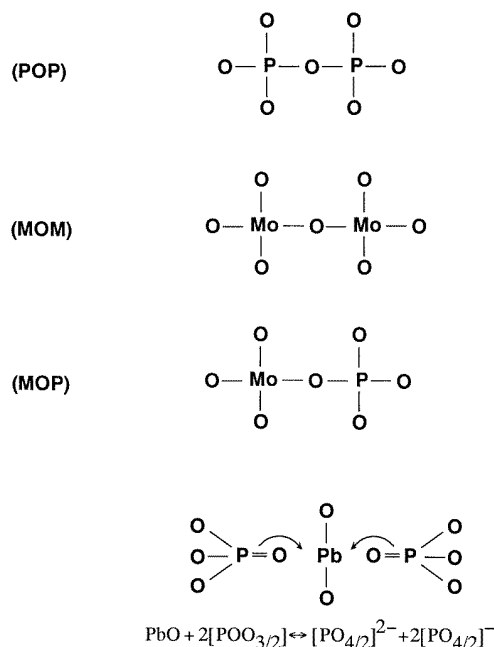


Figure 7. Schematic diagram illustrates the various linkages of the type P–O–P (POP), Mo–O–Mo (MOM), Mo–O–P (MOP) with only bridging oxygen atoms and formation of PbO_4 units in lead molybdophosphate glasses [27, 28, 42].

From the structure point of view [28, 42], it should be noted that when PbO enters the molybdophosphate network, $[\text{PbO}_{4/2}]^{2-}$ pyramidal units are expected to be formed along with the various forms of structural units as shown in figure 7. The substitution of PbCl_2 for PbO will result in not only decreasing the concentration of PbO_4 units but also increases the ability of lead to enter the network as charge carriers. Consequently, the mobility of Pb^{2+} ion increases and in turn enhancement of conductivity is probably expected in the present glasses. Then the overall effects of PbCl_2 substitution for PbO appear to increase not only the number of Pb^{2+} as charge carriers but also its mobility. Based on the above findings I expect that a highly expanded network structure provides easy pathways for ion migration.

The conductivity enhancement would generally be dominated by decreasing the associated activation energy for conduction E_a (figure 5), since accommodation of chlorine ions in glasses is expected to decrease the jump distance of Pb^{2+} ions and open up the glass network. Then the structure is weakened and this is evident in the production of easily conducting pathways for Pb^{2+} ions. The migration of Pb^{2+} ions is then thought to occur in this preferential pathway of low activation energy made up by Cl^- ions. Therefore, increasing the additional migration pathways is considered to be the dominant factor affecting not only the increment in conductivity but also decreasing the activation energy for Pb^{2+} cations. The decreasing trend

in E_a with PbCl_2 content is probably due to the decreasing compactness of the glass structure as the number of PbO_4 units decreases. Hence, the charge carriers are able to pass more easily which leads to a significant decrease in E_a .

From a conduction point of view, to identify the status of glasses in the present study, it is important to make a comparison between the values of conductivity of these glasses and that of glasses for a corresponding series of lead halogenated borophosphate glasses [10], see figure 6. It is clear from figure 6 that the present quaternary glass system (open circles) shows a higher conductivity than that of lead borophosphate glasses (open triangles) containing PbCl_2 . These results show that the molybdenum-based phosphate network is relatively less resistive to transport Pb^{2+} ions than another mixed glass network [10] and almost than the individual ternary ones containing PbCl_2 [3, 41, 43].

5. Conclusion

The glass formation was considered in a wide range of substitution of PbO by PbCl_2 at a constant total content of glass-forming oxide. Several effects of composition on the thermal and physical properties (T_g , α , H_v , V_m and σ) of the present quaternary PbCl_2 - PbO - MoO_3 - P_2O_5 glass system have been examined and discussed. A dramatic increase is found in the thermal expansion coefficient α , molar volume V_m and ionic conductivity σ as PbCl_2 replaces PbO . Moreover, T_g and H_v showed a remarkable decrease.

Correlating these observations, it is concluded that the conductivity behaviour observed in the present glasses is related to increasing expansion upon PbCl_2 addition, which is related to the formation of additional pathways in the network accounting for increase of the mobility of Pb^{2+} ions. The obtained data may lead to useful information on the applicability of these materials in certain devices in the field of electrochemical applications.

The conductivity of the present quaternary MoO_3 -based phosphate glass system containing PbCl_2 is higher than those of glasses based on the B_2O_3 - P_2O_5 system.

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References

- [1] Silim H A, El-Damrawi G, Moustafa Y M and Hassan A K 1994 *J. Phys.: Condens. Matter* **6** 6196
- [2] Rao K J, Wong J and Rao B G 1984 *Phys. Chem. Glasses* **25** 57
- [3] El-Damrawi G 1994 *J. Non-Cryst. Solids* **176** 91
- [4] Kamitsos E I, Kapoutsis J A and Chryssikos G D 1995 *Phys. Chem. Glasses* **36** 141
- [5] Stangrenec M K and Elliot S R 1994 *Solid State Ion.* **73** 199
- [6] Hu L and Jaig Z 1994 *Phys. Chem. Glasses* **35** 38
- [7] Kawamura J and Shimoji M 1986 *J. Non-Cryst. Solids* **88** 281
- [8] Rousselot C, Malugani J P, Mercier R and Ingram M D 1995 *Solid State Ion.* **78** 211
- [9] Massot M, Souto S and Balkanski M 1995 *J. Non-Cryst. Solids* **182** 49
- [10] El-Damrawi G, 1995 *J. Phys.: Condens. Matter* **7** 1557
- [11] El-Damrawi G, Hassan A K and Meikhail M S 1996 *Phys. Chem. Glasses* **37** 101
- [12] Machida N, Kawachi M, Ueda A, Shigematsu T, Nakanishi N, Takahashi M and Minami T 1995 *Solid State Ion.* **79** 273
- [13] Satyanarayana N and Radhakrishna S 1988 *Solid State Ion.* **28-30** 811
- [14] Bunda F, Constantini A and Buri A 1992 *Phys. Chem. Glasses* **33** 40

- [15] Chowdari B V R and Gopalakrishnan R 1988 *J. Non-Cryst. Solids* **105** 269
- [16] Kawamoto Y, Kanno R, Ogura K and Shojiya M 1994 *Phys. Chem. Glasses* **35** 216
- [17] Xihuai H and Pengnian H 1982 *J. Physique* **43** 415
- [18] Tsai P P and Greenblatt M 1988 *J. Non-Cryst. Solids* **103** 101
- [19] Ahmed A A, Abbas A F and Salman S M 1985 *Phys. Chem. Glasses* **26** 17
Doweidar H, El-Damrawi G, Moustafa Y M and Hassan A K 1999 *Phys. Chem. Glasses* at press
- [20] Chowdari B V R and Akhter S K 1988 *Solid State Ion.* **28-30** 747
- [21] Wong J and Angel C A 1976 *Glass Structure by Spectroscopy* (New York: Dekker)
- [22] Villa M, Chiodelli G and Seagliotti 1986 *Solid State Ion.* **18/19** 382
- [23] Welles A F 1975 *Structural Inorganic Chemistry* (Oxford: Oxford University Press)
- [24] Bridge B and Patel N D 1986 *J. Mater. Sci.* **21** 1187
- [25] Selvaraj U, Kershava Sundar H G and Rao K J 1989 *J. Chem. Soc. Faraday Trans. I* **85** 251
- [26] Chowdari B V R, Tan K L, Chia W T and Gopalakrishnan R 1991 *J. Non-Cryst. Solids* **128** 18
- [27] Jamniky M, Znasik P, Tunega D and Ingram M D 1995 *J. Non-Cryst. Solids* **185** 151
- [28] Selvaraj U and Rao K J 1988 *J. Non-Cryst. Solids* **104** 300
- [29] Ray N H, 1974 *J. Non-Cryst. Solids* **15** 423
- [30] Prod'home M 1968 *Phys. Chem. Glasses* **9** 101
- [31] El-Batal H A, Ghoneim N A and Nassar A M A 1983 *J. Non-Cryst. Solids* **55** 343
- [32] Ghoneim N A and El-Badry Kh 1983 *Thermochim. Acta* **60** 252
- [33] Takamori T, Reisman A and Berkenblit M 1976 *J. Am. Ceram. Soc.* **59** 312
- [34] Chopra N, Mansingh A and Mathur P 1992 *J. Non-Cryst. Solids* **146** 216
- [35] Uhlman D R and Shaw R R 1969 *J. Non-Cryst. Solids* **1** 347
- [36] Doi A 1994 *Phys. Chem. Glasses* **35** 34
- [37] Schleitveiler P M and Johnson W B 1986 *Solid State Ion.* **18/19** 393
- [38] Cameron G G, Harrie J L and Ingram M D 1989 *Faraday Discuss. Chem. Soc.* **88** 1
- [39] Bruce P G, Hardgrave M T and Vincent C A 1992 *Solid State Ion.* **53-56** 1087
- [40] Harton M and Shelby J E 1993 *Phys. Chem. Glasses* **34** 238
- [41] Sundar H G K, Martin S W and Angell C A 1986 *Solid State Ion.* **18/19** 437
- [42] Boudlich D, Haddad M, Nadiri A, Berger R and Kliava J 1998 *J. Non-Cryst. Solids* **224** 135
- [43] Magistris A and Chiodelli G 1983 *Solid State Ion.* **9/10** 611