Thermal and optical properties of ternary NaPO$_3$-KHSO$_4$-MCl$_2$ (M = Pb, Zn and Cd) glasses

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Sulfophosphate glasses containing MCl$_2$ (M=Pb, Zn and Cd) have been synthesized in the NaPO$_3$- KHSO$_4$- MCl$_2$ systems. Large vitreous areas are observed and samples 1 cm in thickness have been obtained. These glasses are stable at room atmosphere and soluble in water. Characteristic temperatures for glass transition (Tg) and onset of crystallization (Tx) have been measured. Tg ranges between 180 and 245 °C. Refractive index has been measured between 633 nm and 1551 nm. It is close to 1.5.

1. Introduction

Phosphate glasses have been extensively studied and used as hosts for rare earths, leading to various active optical components. Most of these glasses are based on metaphosphates with the general formula M(PO$_3$)$_n$, for example NaPO$_3$, Ba(PO$_3$)$_2$, Al(PO$_3$)$_3$[1]. The n value corresponds to the valence of the M metal. Numerous glass compositions based on sodium polyphosphate have been investigated. They appear as low melting glasses that exhibit lower characteristic temperatures than classical oxide glasses. Other features include higher thermal expansion and larger sensitivity to water. This behaviour is usually perceived as a severe limitation to practical applications. Structure of phosphate glasses is described on the basis of the connection between PO$_4$ tetrahedra. In this respect the ^{31}P NMR makes a powerful tool for structural investigations.

Sulphate glasses make a group of exotic glasses that have been studied for basic science purposes. They are often considered as glasses from molten salts. The mechanism of glass formation in these glasses raises questions as there is no evidence for any "vitreous network", which is currently viewed as a prerequisite for glass existence. While many sulphate glasses are prone to devitrification, numerous vitreous systems have been reported so far. Potassium hydrogenosulfate (KHSO$_4$) was obtained in the vitreous form by Forland and Weyl sixty years ago [2]. Binary glasses in the ZnSO$_4$-K$_2$SO$_4$ system have been the subject of several studies [3-5]. Other zinc sulfate glasses were reported in the TlSO$_4$-ZnSO$_4$ [3] and (NH$_4$)$_2$SO$_4$-ZnSO$_4$ [6] systems. Optical transmission and thermal properties [7,8] have been investigated. The evolution of viscosity versus temperature strongly deviates from arrhenian law and it does not follow the Vogel-Fulcher-Tamman relation. According to Angell, this behaviour corresponds to "fragile" glasses[9]. Not surprisingly, mechanical properties and chemical durability are limited. The spectroscopy of lanthanide ions in potassium and zinc sulphate glasses has been the subject of several papers [10,11]

Chloride incorporation can increase glass forming stability as exemplified by the K$_2$SO$_4$-CoCl$_2$ system [4]. Sulphate glasses can accommodate classical glass formers such as phosphorus oxide. For example, glasses in the P$_2$O$_5$-ZnSO$_4$-K$_2$SO$_4$-LiSO$_4$ system have been studied as host for organic molecules and polymers[12]. The spectroscopic properties of the Nd^{+3} ions in the vitreous system (88-x) P$_2$O$_5$-xNa$_2$SO$_4$-10BaF$_2$-2NdF$_3$ were reported by G.A. Kumar[13]. The influence of sulphate addition on glass structure has been studied in the Na$_2$PO$_3$-Na$_2$SO$_4$ system[14] and in iron phosphate glasses[15-16]. More recently structure and mechanical properties of (Na,Zn) sulfophosphate glasses have been reported [17,18]. The chemical durability and the thermal properties of iron phosphate glasses containing sulphates were studied in the system [(1-x)-(0.6P$_2$O$_5$-Fe$_2$O$_3$)].x Ry SO$_4$ (R=Li, Na, K, Mg, Ba, Pb) [15]. Such glasses could be used for the nuclear waste containment, with chemical resistance comparable with that of silicates[16]. There are also reports of lithium and sodium ionic conductivity in sulfophosphate glasses[19,20]. Electric properties of binary NaPO$_3$-KHSO$_4$ glasses have been reported in a previous paper[21].

This paper is centred upon new sulfophosphate glasses containing dichlorides MCl$_2$ (M=Pb, Zn and Cd). The NaPO$_3$-KHSO$_4$ system was chosen as the basis for ternary systems because both NaPO$_3$ and KHSO$_4$ can exist in the vitreous form. Zinc chloride may also form a glass while cadmium and lead chlorides have been reported as glass progenitors [22-24]. The first aim of this study is to collect data that could help to understand the mechanism of glass formation. Potential applications and developments are also considered.

2. Experimental

2.1. Glass synthesis

Starting materials used for preparation are commercial products: sodium polyphosphate $NaPO_3$ (97% Rectapur from WWR Prolabo), potassium hydrogenosulfate $KHSO_4$ (99% Rectapur from WWR Prolabo), lead chloride $PbCl_2$, zinc chloride $ZnCl_2$ and cadmium chloride $CdCl_2$ (99, 9%) from Aldrich.

Glasses are prepared at room atmosphere by melting, fining, and casting[25,26]. The calculated amount of the starting materials is introduced in a silica crucible. After melting is completed, a clear liquid is obtained. Then this liquid is briefly heated at a higher temperature for the fining step and cooled inside the crucible at a temperature low enough to increase viscosity.

Afterwards, the melt is cast into a brass mould preheated below the glass transition temperature Tg (Tg-10ºC). Annealing is implemented at this temperature for several hours in order to minimize mechanical stress resulting from thermal gradients upon cooling. Finally, bulk samples are cut and polished.

2.2. Characterizations

Characteristic temperatures (Tg for glass transition, Tx for onset of crystallization and Tp for maximum of crystallization peak) were determined by differential scanning calorimeter (DSC) using a DSC Q20 TA instrument set-up. The estimated error or the temperature is 2°C for glass transition and onset of crystallization which are obtained from tangents intersection and 1°C for the position of the crystallization peak.

Samples, 10-20 mg in weight, were set in aluminium pans and heated at10 K/min heating rate.

The stability of the glasses with respect to devitrification is evaluated using the stability factors $\Delta H = Tx-Tg$ [27] and S [28], defined as follows:

$$\Delta H = Tx-Tg \qquad\qquad S= (Tx-Tg)(Tp-Tx)/Tg$$

The measure of the refractive index is implemented using a METRICON model 2010 prism coupler. Refractive index is measured at various wavelengths. The 2010/M model comprises several laser sources in the 400-1600 nm range. The wavelengths used for refractive index measurements are: 633, 830, 1061, 1310 and 1550 nm.

3. Results

3.1. Glass formation

Three ternary systems were investigated: $NaPO_3$-$KHSO_4$-$PbCl_2$, $NaPO_3$-$KHSO_4$-$ZnCl_2$ and $NaPO_3$-$KHSO_4$-$CdCl_2$. Fig. 1 reports the various compositions investigated in these systems and the corresponding limits of the vitreous domains. However, in the ternary system containing lead chloride the vitreous area is smaller than in the systems with zinc chloride and cadmium chloride. In all cases, vitreous zone extends beyond 50 mol% $NaPO_3$.

The limits for glass formation depend on cooling rate. Larger cooling rates are required when devitrification rate increases, that is for the less stable glasses corresponding to the limits of the vitreous area. Note that $NaPO_3$ itself may form a glass at moderate cooling rate. In this study, samples of 1 cm in thickness are obtained in many cases, simply by pouring the melt in preheated brass moulds. Large samples can be prepared from these glasses, but, depending on composition, they may be very sensible to moisture, especially with zinc chloride.
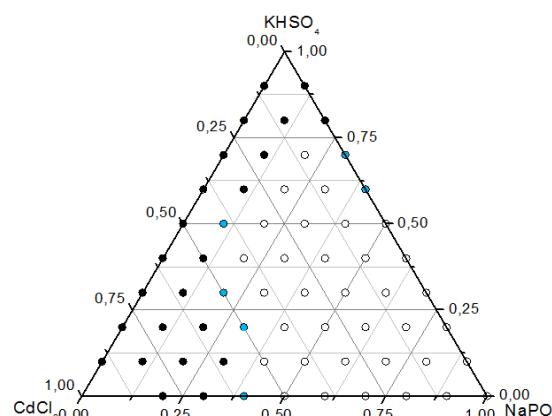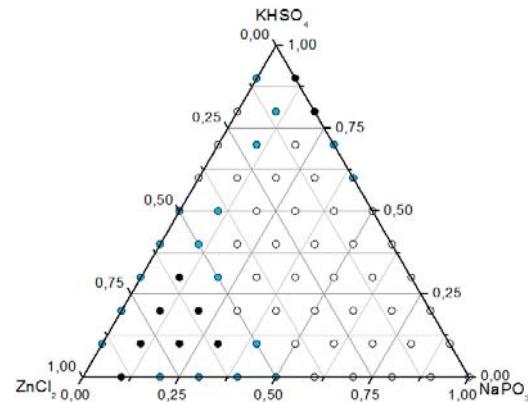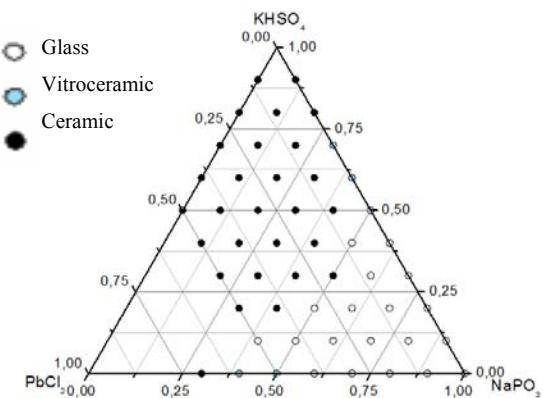

Fig. 1. Glass forming areas in the $NaPO_3$-$KHSO_4$-$PbCl_2$, $NaPO_3$-$KHSO_4$-$ZnCl_2$ and $NaPO_3$-$KHSO_4$-$CdCl_2$ ternary systems.

3.2. Physical properties

3.2.1. Thermal properties

Characteristic temperatures -Tg for glass transition, Tx for onset of crystallization, Tp for maximum of crystallization exotherm- have been measured by DSC for these ternary glasses. Corresponding values are given in table 1 that also reports the stability factors ΔH and S from which relative stabilities are estimated. The general trend is that chloride incorporation leads to the decrease of the glass transition temperature. The variation of the characteristic temperatures with composition is exemplified by figure 2.

Table. 1. Characteristic temperatures and stability factors of sulfophosphate glasses

Glass composition	Tg(°C)	Tx(°C)	Tp(°C)	Tx – Tg(°C)	S(K)
70NaPO$_3$20KHSO$_4$10PbCl$_2$	214	294	314	80	7.5
60NaPO$_3$20KHSO$_4$20PbCl$_2$	219	258	272	39	2.5
50NaPO$_3$20KHSO$_4$30PbCl$_2$	200	231	242	31	1.7
50NaPO$_3$10KHSO$_4$40PbCl$_2$	194	254	269	60	4.6
40NaPO$_3$10KHSO$_4$50PbCl$_2$	181	232	246	51	3.9
70NaPO$_3$20KHSO$_4$10ZnCl$_2$	214	298	318	84	7.8
60NaPO$_3$20KHSO$_4$20ZnCl$_2$	212	289	315	77	9.4
50NaPO$_3$20KHSO$_4$30ZnCl$_2$	208	322	334	114	6.6
40NaPO$_3$20KHSO$_4$40ZnCl$_2$	200	242	281	42	8.2
30NaPO$_3$20KHSO$_4$50ZnCl$_2$	155	172	194	17	2.4
70NaPO$_3$20KHSO$_4$10CdCl$_2$	244	335	381	81	13.4
60NaPO$_3$20KHSO$_4$20CdCl$_2$	242	361	384	109	9.9
50NaPO$_3$20KHSO$_4$30CdCl$_2$	240	346	379	106	14.5
40NaPO$_3$20KHSO$_4$40CdCl$_2$	238	313	329	72	4.8
40NaPO$_3$10KHSO$_4$50CdCl$_2$	235	316	334	81	6.2
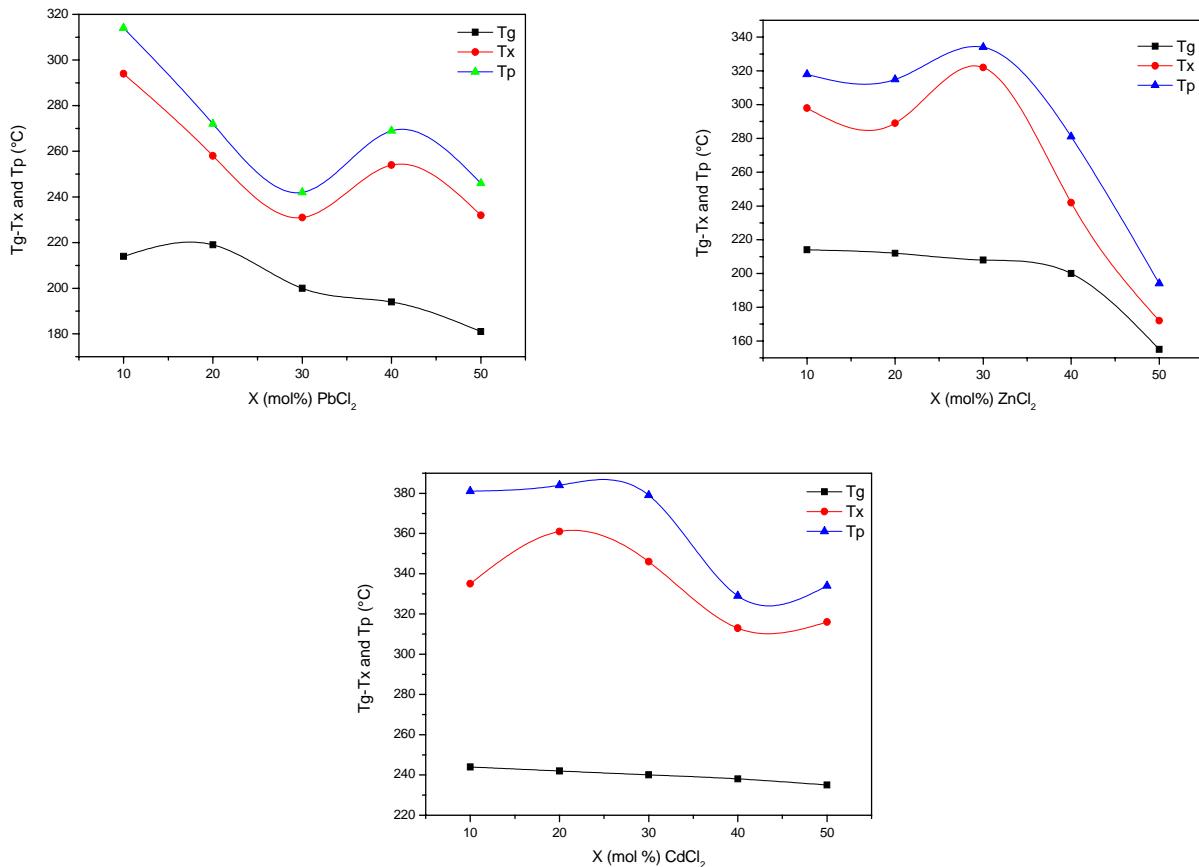
Fig. 2. Variation of characteristic temperatures versus composition parameter x in (80-x)NaPO$_3$-20KHSO$_4$-xPbCl$_2$ (a), (80-x)NaPO$_3$-20KHSO$_4$-xZnCl$_2$ (b) and (80-x)NaPO$_3$-20KHSO$_4$-xCdCl$_2$ ternary glasses

3.2.2. Optical Properties

Optical transmission range extends from 350 nm in the near UV to 2.5 μm in the mid Infrared. On the short wavelength side, it is limited by cationic impurities (e.g. Fe, Cr, Ni, Cu). Infrared cut-off arises from the large OH absorption around 3 μm.

Refractive index depends on two factors: the polarizability of the ions and the chemical bonds, and the number of polarizable elements per unit of volume. Three glass samples from these systems have been prepared with the same molar concentrations: $70NaPO_3-20KHSO_4-10PbCl_2$, $70NaPO_3-20KHSO_4-10ZnCl_2$ and $70NaPO_3-20KHSO_4-10CdCl_2$. Refractive index n has been measured for different wavelengths: 633, 830, 1310 and 1550 nm. Results are gathered in Table 2. The n values are close to 1.5, with smaller value for zinc-containing glass and larger value with lead. They decrease as wavelength increases. Consequently Fresnel losses are small and optical non linearity is expected to be very low.

Table. 2. Refractive index versus wavelength λ of $70NaPO_3-20KHSO_4-10PbCl_2$, $70NaPO_3-20KHSO_4-10ZnCl_2$ and $70NaPO_3-20KHSO_4-10CdCl_2$ glasses

λ (nm)	n_D (NKPb)	n_D (NKZn)	n_D (NKCd)
632.8	1.5280	1.4888	1.4977
825	1.5213	1.4843	1.4932
1060.7	1.5192	1.4816	1.4916
1311	1.5171	1.4789	1.4874
1551	1.5135	1.4761	1.4862

4. Discussion

As one could expect, bulk glass samples have been obtained in these systems associating sodium polyphosphate, potassium hydrogenosulphate and divalent chlorides. The extent of the vitreous areas is consistent with the glass forming ability of the three components, even though only pure $NaPO_3$ appears as a glass in the present synthesis conditions. Anhydrous atmosphere is required to obtain vitreous $ZnCl_2$. One should also point out that these glasses could be prepared by soft chemistry route, using coacervates. As an example, the $NaPO_3$-$ZnCl_2$-H_2O and $NaPO_3$-$ZnSO_4$-H_2O systems have been investigated[29]. However chlorine content is more difficult to control.

Thermal properties are strictly correlated to composition. While glass transition temperature Tg is 262 °C in pure $NaPO_3$ glass, incorporation of $KHSO_4$ and/or MCl_2 chlorides leads to the significant decrease of Tg, in the 200-240°C range in most cases. This decrease results from the changes in network connectivity. The structural units MO_4 are usually separated in Q^1, Q^2, Q^3 and Q^4 tetrahedra, according to the number of shared corners (bridging oxygens). While polyphosphates exhibit long chains in which PO_4 tetrahedra (Q^2) have two non bridging oxygens, introduction of large isolated SO_3OH tetrahedra and chlorine anions breaks these chains, increasing the relative number of Q^1 tetrahedra at the expense of the original Q^2 tetrahedra. Then solid material becomes more sensitive to thermal motion, which logically decreases Tg value.

Crystallization occurs in the molten state and the temperature range between onset of crystallization and Tg (ΔT=Tx-Tg) provides a qualitative measurement of the stability against devitrification. The rather large values of this thermal stability range are consistent with the maximum thickness of glass samples.

Glasses from these systems exhibit practical limitations -low Tg, water sensitivity, large OH content- that could be turned into advantages for optical fibre technology. The fabrication of coherent fibre bundles is currently implemented from multicore solid preforms that are drawn into a rigid cylinder. These preforms consist in the assembly of waveguides and passive rods soluble in acidic solution. A set of flexible fibres is obtained after etching in an acidic aqueous solution. This process requires that thermal properties of all glass components are compatible in order to have close viscosities at drawing temperature. This requirement applies to chalcogenide glasses that are developed for infrared transmission. Softening temperature of sulphur-free chalcogenide glasses is rather low, and this limits the choice for thermally compatible glasses. The sulfophosphate glasses of this study may be adjusted to the process specifications as they are water soluble with low characteristic temperatures.

The spectroscopy of rare earth ions in glasses has been extensively studied, and there is some emphasis on the phonon energy of the glass host. Low phonon energy reduces transfer between close energy levels. This may be critical for some laser applications, for example praseodymium-based fibre amplifiers at 1.3 μm [30]. On the other hand, some transitions are almost insensitive to this phonon energy. This is the case for Yb^{3+} emission around 1 μm. With $KHSO_4$ as a glass component, hydroxyl concentration is large. As OH phonon energy is close to 3100 cm^{-1} it will enhance the quenching of many active levels that could emit in the IR spectrum. This applies to several rare earth ions, in particular Er^{3+} emission at 1.5 μm.

5. Conclusion

New vitreous systems based on the $KHSO_4$ - $NaPO_3$ association have been investigated and characterized. Stable bulk samples are obtained beyond 50 mol % $NaPO_3$. The incorporation of $PbCl_2$, $ZnCl_2$ and $CdCl_2$ in the basic binary system allows some variation of the physical properties.

The substitution of $NaPO_3$ by $PbCl_2$, $ZnCl_2$ and $CdCl_2$ decreases glass transition temperature Tg. Refractive index has been measured for several wavelengths between 633

nm and 1551 nm; it is close to 1.5. These glasses are water soluble. They could be used in fibre optics technology. Their high concentration in hydroxyls gives this glass host a very large phonon energy that may be used for quenching selected transitions in rare earth ions.

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