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Physical properties of ternary NaPO3-KHSO4-MX (M=Na, K and X=Cl, Br) glasses

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Abstract

This contribution focusses on some thermal, optical and mechanical properties of sulfophosphate glasses containing MX (M=Na, K and X=Cl, Br) synthesized in the NaPO3- KHSO4- MX systems. The synthesized samples of 1 cm in thickness present large vitreous areas. These glasses are stable at room atmosphere and soluble in water. Characteristic temperatures of glass transition and onset of crystallization were measured. The temperature of glass transition and the coefficient of thermal expansion range between 180 and 254 °C and between 217.10-7 k-1 and 270.10-7k-1, respectively. Refractive index of all the samples is found is close to 1.48 in the 633-1555 nm wavelength range. The micro hardness and the elastic moduli of the samples were also measured.

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Keywords: Sulfophosphate glasses; Thermal expansion; Microhardness; Elastic moduli; Refractive index

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 met phosphates 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

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exhibit lower characteristic temperatures than classical oxide glasses. Other features include higher thermal expansion and larger sensitivity to water. This behavior 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_2SO_4 system have been the subject of several studies [3-5]. Other zinc sulfate glasses were reported in the $TISO_4$-$ZnSO_4$ [3] and $(NH_4)_2SO_4$-$ZnSO_4$ [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 behavior 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_2SO_4-$CoCl_2$ system [4]. Sulphate glasses can accommodate classical glass formers such as phosphorus oxide. For example, glasses in the P_2O_5-$ZnSO_4$-K_2SO_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_2O_5-xNa_2SO_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_2PO_3-Na_2SO_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_2O_5-Fe_2O_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 centered upon new sulfophosphate glasses containing MX (M=Na, K and X=Cl, Br). The $NaPO_3KHSO_4$ system was chosen as the basis for ternary systems because both $NaPO_3$ and $KHSO_4$ can exist in the vitreous form. Sodium and Potassium halogen 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.

These glasses associate high transparency in the visible-NIR spectrum with the significant hydrogen mobility resulting from the incorporation of potassium hydrogenosulfate. This new vitreous material opens prospects for solar cells and batteries.

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), Sodium and Potassium chloride NaCl, KCl, Sodium and Potassium bromide NaBr, KBr (99, 98%) 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 into the crucible at a temperature low enough to increase viscosity.

Afterwards, the melt is cooled in 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.

2.1. 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 aluminum pans and heated at10 K/min heating rate.

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

$$\Delta H = Tx - Tg \quad (1)$$

$$S = (Tx - Tg)(Tp - Tx)/Tp \quad (2)$$

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.

Thermal expansion is measured using a TMA TA 2840 set-up, at 2 K/min heating rate, between 100°C and 250°C. The density of some samples was determined using a helium picnometer (Micromeritics, AccuPyc 1330), with accuracy ± 0.001 g/cm^3. Micro-hardness values were taken by Matzuzawa MXT 70 digital micro hardness tester, and the charge was 100 g. UV transmission was recorded on a Brucker Vector 22 spectrometer. Room temperature ultrasonic measurements were performed by the pulse-echo method with a Panamertics model 5800 pulser/receiver with a quartz transducer. Both X-cut transducer and Y-cut transducer (with 10 MHz frequency) were employed for longitudinal modes and for shear modes.

3. Results

3.1. Glass formation

Four ternary systems were investigated: $NaPO_3$-$KHSO_4$-NaCl, $NaPO_3$-$KHSO_4$-NaBr, $NaPO_3$-$KHSO_4$-KCl and $NaPO_3$-$KHSO_4$-KBr. Fig. 1 reports the various compositions investigated in these systems and the corresponding limits of the vitreous domains. However, in the ternary system containing Potassium chloride the vitreous area is smaller than in the systems with Sodium chloride, Sodium bromide and Potassium bromide. 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.

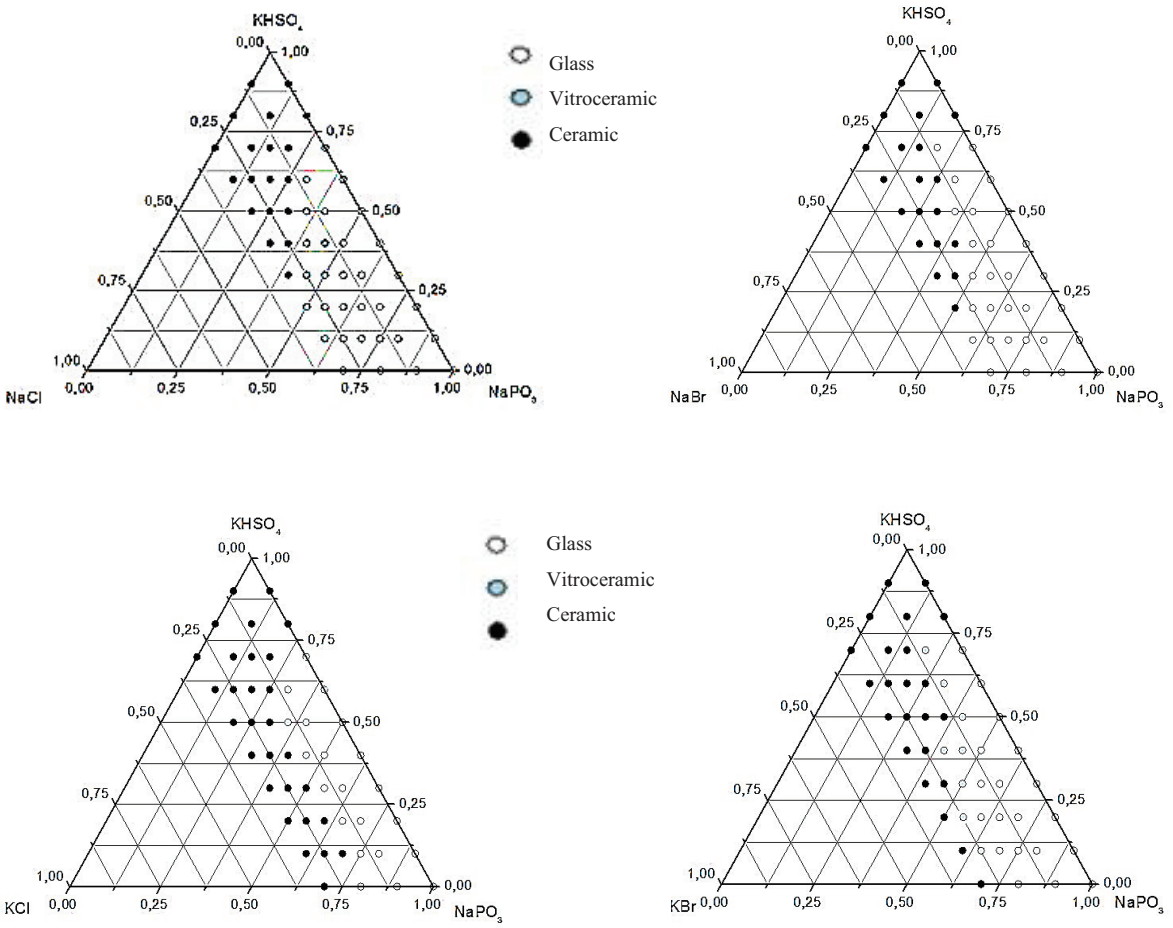

Fig. 1. Glass forming areas in the $NaPO_3$-$KHSO_4$-NaCl, $NaPO_3$-$KHSO_4$-NaBr, $NaPO_3$-$KHSO_4$-KCl and$NaPO_3$-$KHSO_4$-KBr ternary systems.

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 and the coefficient of thermal expansion CTE. The general trend is that halogen incorporation leads to the decrease of the glass transition temperature.

Table 1. . *Coefficient of thermal expansion CTE and characteristic temperatures: T_g for glass transition, T_x for onset of crystallization, T_p for maximum of exotherm. T_x-T_g and S factor are stability criteria*

Glass composition	Tg(°C)	Tx(°C)	Tp(°C)	Tx – Tg(°C)	S(K)	CTE ($10^{-7}K^{-1}$)
55N30K15NaCl	181	239	260	58	6.7	270
55N30K15NaBr	191	235	247	44	2.9	260
55N30K15KCl	254	291	305	37	2.04	253
55N30K15KBr	208	283	312	75	10.46	217

3.2.2. Optical properties

Optical transmission range extends from 300 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, and Cu). Infrared cut-off arises from the large OH absorption around 3µ m.

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. Four glass samples from these systems have been prepared with the same molar concentrations: $55NaPO_3$-$30KHSO_4$-15NaCl, $55NaPO_3$-$30KHSO_4$-15NaBr, $55NaPO_3$-$30KHSO_4$-15KCl and $55NaPO_3$-$30KHSO_4$-15KBr. 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 1.48. They decrease as wavelength increases. Consequently Fresnel losses are small and optical non linearity is expected to be very low.

Table *2. Refractive index at different wavelengths*

λ (nm)	n (55N30K15NaCl)	n(55N30K15NaBr)	n (55N30K15KCl)	n (*55N30K15KBr*)
632.8	1.4780	1.4778	1.4887	1.4967
825	1.4717	1.4735	1.4852	1.4912
1060.7	1.4691	1.4682	1.4796	1.4883
1311	1.4670	1.4665	1.4769	1.4847
1551	1.4635	1.4631	1.4727	1.4811

3.2.3. Mechanical properties

The density ρ is nearly constant for the three glasses, ranging from 2.45 to 2.49 $g.cm^{-3}$.

The values of Young's modulus E, bulk modulus K, shear modulus G and Poisson ratio µ have been calculated from the measured longitudinal and transverse sound velocities V_L and V_T. Table 3 reports the corresponding values to the $60NaPO_3$20$KHSO_4$20NaBr composition. The experimental microhardness measured by Vickers indentation is given in table 4.

Table *3. Density, sound velocity and elastic moduli*

Acronym	ρ (Kg/m3)	V_L (m/s)	V_T (m/s)	E (GPa)	G (GPa)	K (GPa)	µ
60N20K20NaBr	2452	4234	2252	32.39	12.43	27.4	0.303

Table *4. Vichers microhardness*

Acronym	55N30K15NaCl	55N30K15NaBr	55N30K15KCl	*55N30K15KBr*
Hv(Kg/mm^2)	157	74	67	123

4. Discussion

Bulk glass samples are obtained in these systems associating sodium polyphosphate, potassium hydrogen sulphate and monovalent chlorides and bromides. The extent of the vitreous areas is consistent with the glass forming ability of the four components, even though only pure $NaPO_3$ appears as a glass in the present synthesis conditions. 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 MX (X=Cl,Br) leads to the significant decrease of Tg, in the 200250°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 and bromine anions break 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 ($\Delta T=Tx-Tg$) 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 fiber 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 is 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 □m. 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 NaCl, NaBr, KCl and KBr in the basic binary system allows some variation of the physical properties. These glasses associate high transparency in the visible-NIR spectrum with the significant hydrogen mobility resulting from the incorporation of potassium hydrogenosulfate. This new vitreous material opens prospects for solar cells and batteries.

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