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Fluorophosphate Glasses containing Manganese

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Abstract

New fluorophosphate glasses based on MnF_2 , NaPO_3 and MF_n ($M = \text{Zn}^{2+}$, Sr^{2+} , Mg^{2+} , Ba^{2+} , Li^+ , Na^+ and K^+) have been synthesised and characterized. Large vitreous areas were observed. Samples of 4 mm in thickness have been obtained. These glasses are easy to prepare and stable in ambient air. Depending on the composition and the nature of the M cation, glass transition temperature, T_g , lies between 230 and 314°C, crystallisation temperature, T_x is between 320 and 475°C. These glasses are pink coloured, and infrared transmission extends up to 4.5 μm with extrinsic OH^- absorption band at 3200 cm^{-1} and other bands around 2200 and 1600 cm^{-1} that relate to PO_4 tetrahedron vibration. Other physical properties including density, microhardness, Young modulus, thermal expansion and refractive index were investigated and correlated to composition.

Key words: fluorophosphate glasses, thermal properties, optical properties, IR transmission, physical properties.

1. Introduction

Numerous fluorophosphate glasses have been studied for their potential applications [1-5]. Most of them are based on alkali, earth alkali or trivalent polyphosphates with the general formula $\text{M}(\text{PO}_3)_n$, with $n = 1, 2$ or 3 . Among other features, they may have a good transmission in the UV spectrum [4] and host rare earth cations, leading to active optical devices.

This study focuses on fluorophosphate glasses containing manganese difluoride MnF_2 , both for fundamental studies and for special optical uses, taking advantage of fluorescence and magnetic properties of divalent manganese.

The starting point of our work is the glass formation in binary fluoride systems that combine MnF_2 with other fluorides [6]. While such glasses have been characterized, their stability against devitrification is limited as they require fast cooling rates, which does not allow thick samples to be obtained. The incorporation of sodium polyphosphate $(\text{Na}(\text{PO}_3))_n$

appears as a simple way to increase glass stability, as this has already been reported in the $\text{Na}(\text{PO}_3)\text{-BaF}_2\text{-MnF}_2$ ternary system [7]. This additive keeps a low temperature of melting, which limits fluorine losses that occur with the formation of gaseous POF_3 . While pure $\text{Na}(\text{PO}_3)$ glass is somewhat sensitive to water, the incorporation of insoluble fluoride increases chemical durability, especially in wet atmosphere: sample surface remains clear even at high relative humidity.

The systematic investigation of the glass forming ranges in the ternary systems $\text{MnF}_2\text{-NaPO}_3\text{-MF}_n$ ($M = \text{Zn}^{2+}, \text{Sr}^{2+}, \text{Mg}^{2+}, \text{Ba}^{2+}, \text{Li}^+, \text{Na}^+$ and K^+) has been carried out. The evolution of the physical properties versus chemical composition has also been implemented.

2. Experimental

Starting Materials

Fluorides ZnF_2 , SrF_2 , MgF_2 , BaF_2 , NaF , LiF and KF are commercial products from ALDRICH and WWR, with a 99.9 % purity. Ammonium hydrogenofluoride $\text{NH}_4\text{F.HF}$ is from Riedel de Haen and from WWR (Prolabo).

Manganese difluoride has been synthesized in the laboratory, using MnO and $\text{NH}_4\text{F.HF}$ as a fluorinating reagent in a platinum crucible, and controlled by X-Ray diffraction.

Glass synthesis

Glasses are prepared at room atmosphere using the ammonium bifluoride processing [8]. The calculated amount of the starting materials is introduced in a long platinum crucible with an excess of $\text{NH}_4\text{F.HF}$. This reagent acts as a fluorinating reagent to convert oxides in fluorides and also to protect the melt from atmospheric hydrolysis. After melting is complete, a clear liquid is obtained. Then this liquid is briefly heated at higher temperature for the fining step and cooled into the crucible to a temperature low enough to have larger viscosity without visible crystallization. Finally it is cast onto a brass mould and squeezed by another metallic plate. The resulting sample corresponds to a “quenched glass”; its thickness lies between 0.4 and 1 mm, and effective cooling rate may reach 1000 K.s^{-1} . Thicker samples are obtained when melt is cast between two brass walls that are heated at temperature close to T_g . A final annealing stage is carried out for 6 hours at temperature : $T_a = (T_g - 10)^\circ\text{C}$, to remove residual thermal stresses prior to polishing.

Characterizations

Characteristic temperatures (T_g for glass transition, T_x for onset of crystallization and T_p for maximum of crystallization peak) were determined by differential scanning calorimeter (DSC) using a SEIKO DSC/220 set-up. The estimated error on the temperature is 2 K for glass transition and onset of crystallization which are obtained from tangents intersection and 1 K for the position of the crystallization peak. Samples, 10 to 20 mg in weight, were set in aluminum pans under N_2 atmosphere at 10 K/min heating rate.

Thermal expansion is measured using a TMA 2840 (TA Instruments) set-up, at 2 K/min heating rate, between 50°C and 200°C . Estimated experimental error is $\Delta\alpha = \pm 2 \times 10^{-7} \text{ K}^{-1}$. The densities were determined by gas pycnometry using He (Micromeritics Accupyc), with a precision of about 10^{-4} . Microhardness (Vickers) is measured using a Matsuzawa MXT set-up with 50 g applied load for 10 seconds. A mean value is obtained after averaging several

measurements. Young (E), Shear (G) modulus, and Poisson ratio (ν) of samples are obtained from ultrasonic measurements using the ultrasonic pulse-echo method.

Infrared transmission spectra were recorded with a BOMEM Michelson Spectrophotometer in the 5000-2000 cm^{-1} range. Glass samples were either plates, 1 to 3 mm in thickness, or powdered glass in KBr pellets. UV transmission between 300 and 500 nm was studied using a Varian spectrophotometer Cary 5. In both cases, data were given directly in transmittance and/or absorbance. Refractive index in the visible spectrum, n_D ($\lambda = 0.5893 \mu\text{m}$), was measured using an Abbe refractometer.

The chemical composition of glasses has been checked by element analysis using energy dispersion spectrometry EDS (Oxford Link ISIS) set-up incorporated into the ISM 6400 Jeol scanning electron microscope.

3. Results

3.1 Glass formation in the MnF_2 - NaPO_3 - MF_n ternary systems.

- *Vitreous areas*

Glass forming ranges have been investigated in ternary systems MnF_2 - NaPO_3 - MF_n ($M = \text{Zn, Sr, Mg and Ba; Li, Na and K}$). Experimental results are gathered in Fig. 1a-g. Glass formation limits depend on cooling rate. Larger cooling rates are required when devitrification rate increases, that is for less stable glasses. Note that NaPO_3 itself may form a glass, and consequently makes the starting point for all vitreous areas.

Manganese-containing glasses are pink and become darker at higher Mn content. Samples are stable at room atmosphere, except for a few compositions with high NaPO_3 concentration and MnF_2 content lower than 5 %.

- *Glass compositions*

The chemical composition of the samples is defined by the relative amount of the starting materials. Taking into account the processing temperature, cations ($\text{Na, Mn, Zn, K, Sr, Ba}$) will not enter the gaseous phase. However there may be exchanges with atmosphere based on oxidation, hydrolysis and volatilization, especially HF and POF_3 molecules may form. Analyses have been carried out on some samples to compare nominal and real compositions. As reported in table 1 for a typical sample, the discrepancy between expected and observed values is limited. Complementary analyses emphasize that phosphorus and fluorine losses are not significant.

3.2 Thermal Properties

3.2.1 Glasses in the MnF_2 - NaPO_3 - ZnF_2 system

Glass stability versus devitrification may be estimated from the characteristic temperatures measured by DSC. While this assessment is not always accurate, it is widely acknowledged that the T_x - T_g difference between the temperature of glass transition and the onset of crystallization is strongly correlated to crystallization tendency [9]. Systematic measurements have been implemented on glasses from the MnF_2 - NaPO_3 - ZnF_2 system. Typical DSC curves appear in figures 2. The evolution of glass transition temperature T_g and thermal stability

range Tx-Tg vs composition is exemplified in figure 3 for two sets of glasses containing 10 and 20 % mol ZnF_2 respectively, in which manganese fluoride replaces sodium metaphosphate NaPO_3 . The general trend is that Tg decreases and Tx-Tg increases when NaPO_3 is incorporated at the expense of MnF_2 .

3.2.2 Glasses in the 30 MnF_2 -50 NaPO_3 -20 MF_n system

A second set of characterizations has been implemented on ternary fluorophosphate glasses with the general formula 30 MnF_2 -50 NaPO_3 -20 MF_n ($M = \text{Li, Na, K, Zn, Sr, Ba, Mg}$). Most of these glasses may be obtained as thick samples. Figure 4 makes the comparison between the characteristic temperatures and the stability range of these glasses. The lowest Tg are observed for lithium and zinc fluoride, while maximum stability is obtained with lithium, zinc and barium. Considering the earth alkali cations, the Tg value drops with increasing ionic radius, from 326 °C for Mg to 277 °C for Sr and 268 °C for Ba.

3.2.3 Glasses in the 30 MnF_2 - x NaPO_3 - y MF ($M = \text{alkali metal}$) systems

Another set of thermal measurements has been implemented to find the optimum alkali concentration to be incorporated in the MnF_2 - NaPO_3 binary system. While glass forming range is drawn in Fig. 1e-g, samples have been selected with the composition 30 MnF_2 -(70-x) NaPO_3 -x MF , ($x = 10, 20, 30$). As shown in figure 5, glass transition temperature and stability factor decrease with rising MF content, suggesting that optimum MF concentration is close to 10 %.

According to the confusion principle, glasses more stable against devitrification should be obtained by the addition of two alkali fluorides instead of one. A series of glass samples has been prepared to investigate this possibility according to the composition rule 30 MnF_2 -40 NaPO_3 -(30-x) LiF -x KF . Corresponding thermal data that appear in table 2 confirm that these quaternary glasses are more stable than the basic ternary glass.

Note that Tg increases as K substitutes Li and most stable glasses (i.e. larger thermal stability range) correspond to 10 to 15 % KF content.

3.3 Other physical properties

3.3.1 Density

- *MnF_2 - NaPO_3 - ZnF_2 glass*

Two sets of samples have been prepared according to the general formula : x MnF_2 -(80-x) NaPO_3 -20 ZnF_2 and x MnF_2 -(90-x) NaPO_3 -10 ZnF_2 . From figure 6, it appears that density increases as MnF_2 substitutes NaPO_3 , and this evolution is roughly linear, density ranging from 2.80 and 3.36 g/cm³.

- *MnF_2 - NaPO_3 -MF ($M = \text{Li, K}$) glass*

Alkali-containing glasses have been investigated. Incorporation of heavier alkali cations into MnF_2 - NaPO_3 -MF system leads to decreasing density. Experimental values are reported in table 2 for the 30 MnF_2 -40 NaPO_3 -(30-x) LiF -x KF glasses.

3.3.2 Thermal expansion

As reported in table 3, the coefficient of thermal expansion (CTE) of glasses in the MnF_2 - NaPO_3 - ZnF_2 system is close to $188 \times 10^{-7} \text{ K}^{-1}$ and variations resulting from composition changes are very small: neither the $\text{NaPO}_3/\text{MnF}_2$ nor the $\text{ZnF}_2/\text{MnF}_2$ substitutions influence significantly the CTE. But we can say that it increases slightly with the size of the third cation (Zn, Sr, Ba, K). The largest value is observed with the glass containing BaF_2 . These CTE values are fairly high and compare to those of fluorozirconate glasses.

3.3.3 Mechanical properties

The microhardness “Hv” evolution versus MnF_2 content is shown in figure 7 for a set of samples with the formula: $x\text{MnF}_2$ -(80-x) NaPO_3 -20 ZnF_2 . There is a linear correlation between microhardness and MnF_2 concentration. These values are smaller than those observed for standard fluoride glasses [10].

For the alkali-containing glasses, microhardness increases with the ionic radius of the alkali cation. Indeed, in the glass 30 MnF_2 -40 NaPO_3 -30 MF , the Hv value grows from 179 to 208 kg/mm^2 when potassium replaces lithium.

Sound velocity has been measured in a series of samples with variable manganese content. Young modulus and Poisson ratios are deduced from these measurements. Results are reported in table 4 and show that these moduli are larger at high MnF_2 content. Young modulus ranges between 39 and 60 GPa, which is close to the values measured for fluoride glasses [11].

3.3.4 Chemical durability

Samples are stable at room atmosphere. However, some compositions may be sensitive to high relative humidity, for example the 80 NaPO_3 – 20 ZnF_2 glass and more generally samples with high NaPO_3 concentration. The surface corrosion that occurs may be the result of water condensation. A set of qualitative tests has been implemented on various samples, based on immersion in deionised water at 20 °C for 48 hours. The general trend is that corrosion layer is smaller when manganese fluoride content increases. NaPO_3 , KF and NaF enhance water attack. For example, using the 30 MnF_2 -50 NaPO_3 -20 ZnF_2 composition, the weight loss of a glass sample, 2.6 g in weight and 7 cm^2 in outer surface, is only 1 mg.

3.4 Optical properties

3.4.1 Refractive index

Refractive index has been measured for samples of variable composition in the MnF_2 - NaPO_3 - ZnF_2 system. As shown in figure 8a, it increases from 1.50 to 1.52 when MnF_2 substitutes NaPO_3 . By comparison, alkali-containing glasses have a lower refractive index. For example, we measured $n_D = 1.516$ for 30 MnF_2 -50 NaPO_3 -20 ZnF_2 glass while it is only 1.480 for the 30 MnF_2 -50 NaPO_3 -20KF glass. Higher values are obtained with lithium as this is shown in figure 8b for the 30 MnF_2 -40 NaPO_3 -(30-x) LiF -xKF glasses.

3.4.2 Optical transmission

a) UV-Visible transmission

Divalent manganese induces optical absorption in the UV-visible spectrum. This is exemplified by figure 9 that shows the transmission spectra of samples containing an increasing amount of Mn^{2+} . Binary $\text{NaPO}_3\text{-ZnF}_2$ glass is colourless and the UV cut-off is below 300 nm. The UV absorption edge is shifted towards longer wavelength as MnF_2 concentration increases. Curves show one shoulder at 350 nm and two absorption bands located around 400 and 500 nm that correspond to transitions of Mn^{2+} ions in octahedral sites [12,13].

b) Infrared transmission

• Bulk samples

The transmission spectrum of the $30\text{MnF}_2\text{-}50\text{NaPO}_3\text{-}20\text{ZnF}_2$ glass has been recorded between 100 and 5000 cm^{-1} and is reproduced in figure 10. The thinner sample (dashed line) evidences the complex structure of the absorption bands.

The main features that emerge from this figure are:

- The absorption band around 3200 cm^{-1} that originates from hydroxyl groups.
- An intense band at 2200 cm^{-1} that defines the transmission limit of the sample.
- Another band around 1600 cm^{-1} .

• Powdered samples

Infrared transmission of powdered samples of the same glass in KBr pellets is shown in figure 11. The spectrum is limited to 400 cm^{-1} , as KBr is no more transparent beyond this frequency. The comparison with bulk glass shows that the absorption observed between 1500 and 2500 cm^{-1} corresponds to the first overtones of the fundamental absorption bands of the PO_4 tetrahedra [14,15].

4. Discussion

As one could expect, sodium polyphosphate makes an efficient stabilizer of the fluoride glasses based on MnF_2 . Thick samples can be obtained, which facilitates mechanical and optical measurements.

The evolution of the physical properties versus composition logically relates to the intrinsic features of the chemical elements and also to glass structure. Main elements may be summarized as follows:

- 1) Phosphorus forms tetrahedra PX_4 in which $\text{X} = \text{O}$ or F , predominantly O .
- 2) Manganese and zinc form MnX_6 octahedra ($\text{M} = \text{O}$ or F) and ZnF_6 octahedra respectively [16].
- 3) Sodium is considered as a network modifier, and its coordination number is large in the solid state: from 6 in NaF to 12 in NaWO_3 [17].
- 4) Bond strength of P-O (110 kcal/mol) bond is larger than that of Mn-O , Zn-O and Na-O bonds [18].
- 5) Ionic radii [19] of Mn^{2+} and Zn^{2+} are close: 83 and 72 pm respectively.
- 6) The structure of the polyphosphate glasses is reported to consist of long $(\text{PO}_3)_n$ chains in which tetrahedra - labelled Q^2 in NMR studies - have 2 bridging and 2 non bridging oxygens. These chains bring negative charges that are balanced by the positive anionic charges (e.g. Na^+). Due to the low connectivity of the vitreous network, T_g is usually low: 260°C in vitreous NaPO_3 [20].

- 7) Vibrational spectroscopy, especially infrared transmission, has been used to provide structural information about fluorophosphate glasses. Studies confirm that fluorides lead to the depolymerization of the polyphosphate chains [21-24]. Fluorides are known to lower network connectivity by creating terminal P-F bonds that take place of P-O-P bridges.
- 8) In manganese fluoride glasses, the vitreous network is made from MnF_6 octahedra sharing corners [16]. The connectivity is large to account for the chemical formula: in crystalline MnF_2 , each corner is shared by 3 octahedra, while all fluorine anions are bridging for a MnF_3 network. Non bridging fluorines appear when the network formula is MnF_{3+x} . This large connectivity accounts for the high T_g of these glasses, for example 377 °C for the 70 MnF_2 -30 BaF_2 binary glass [6].

The evolution of the glass transition temperature versus composition is consistent with these statements. Its value depends on the factors that rule the sensitivity of the structure to thermal motion, namely bond strength and network connectivity. The structure of these glasses may be described as a hybrid network constructed from the association of PX_4 tetrahedra and MnF_6 octahedra. In these materials, glass transition temperature is close to 250 °C. In a general way it decreases as NaPO_3 concentration increases (figure 3). Note that T_g of the 80 NaPO_3 -20 ZnF_2 glass is lower than that of pure NaPO_3 . The T_g decrease exemplifies the depolymerisation of the PO_3 chain by fluorine that creates non bridging anions through the formation of PO_3F tetrahedra. As MnF_2 content increases, the concentration of modifying cations (Na^+) decreases and connectivity increases, which logically results in higher T_g . When MnF_2 substitutes NaPO_3 , the evolution of T_g is nearly linear versus MnF_2 content up to 30 mol% (fig.3b). Beyond this value T_g increases faster, which suggests that there is a structural change beyond this limit. This could correspond to the formation of $\text{Mn}(\text{O},\text{F})_6$ octahedra including the non bridging oxygen of the PO_4 tetrahedra. Anyway it also indicates the transition from a chain structure to a tridimensional network. Note also that, for the same nominal composition, glass transition temperature is higher with large and heavy alkali cations (figure 4) and T_g increases as KF substitutes LiF (table 2). The similar trend has been observed in various halide systems [25-27].

While introduction of NaPO_3 clearly improves resistance to devitrification, the stability of the glass versus devitrification is not unambiguously correlated to composition. It rather increases as the number of component increases, in agreement with the confusion principle. This may explain why thermal stability range is smaller with NaF than with LiF and KF (figure 5): sodium from NaPO_3 enters glass composition and NaF incorporation does not increase the number of different cations.

The $\text{MnF}_2/\text{NaPO}_3$ substitution increases microhardness and Young modulus. One may assume that the decrease in the concentration in monovalent cation (Na^+) and linear chain $(\text{PO}_3)^-$ results in larger lattice energy. The larger network connectivity reported above has the same influence.

Density increases as MnF_2 replaces NaPO_3 , which is partly explained by the smaller atomic weight and the larger size of Na by comparison to Mn. In the same way, density increases when zinc content rises from 10 to 20 mol % at the expense of NaPO_3 (figure 6). This evolution is consistent with the density values of the crystalline materials: 2.6 for NaPO_3 , 3.9 for MnF_2 and 4.9 for ZnF_2 [28]. The K/Li substitution also leads to smaller density (table 2). Although the alkali atomic mass of potassium is larger, the size effect is predominant and decreases molar volume.

Optical transmission is restricted to the visible spectrum because the electronic transitions of Mn^{2+} cations in octahedral ligand field lead to strong UV absorption [12,13]. It is limited to 4.5 micrometers in the mid-infrared by the first overtone of the P-O vibrations, as this has been shown in fluoride glasses doped with phosphates [14,15,29].

Thus, these glasses may be used as filters. They contain large amounts of divalent manganese, and further studies could focus on possible magneto-optic or photo-induced phenomena in addition to the more classical fluorescence.

5. Conclusion

Bulk glasses rich in manganese (> 30 mol % MnF_2) have been obtained in the MnF_2 - NaPO_3 - MF_n systems, with $M = \text{Ba, Sr, Zn, Li, Na, K}$. Glass transition temperature is close to 250°C and depends on composition. Main physical properties, including density, refractive index n_D , microhardness, and thermal expansion, have been measured. The incorporation of manganese fluoride at the expense of NaPO_3 leads to the increase of T_g , n_D , E (Young modulus) and microhardness, while chemical durability is enhanced. Optical transmission is limited in the UV spectrum by electronic transitions of Mn^{2+} ions in octahedral environment and in the IR spectrum by the P-O vibrations.

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Tables

Table 1

Comparison between nominal and analysed cationic and anionic compositions for a ternary glass.

<i>Composition</i> (%mol)	<i>Mn</i> (%cat)	<i>Zn</i> (%cat)	<i>Na</i> (%cat)	<i>P</i> (%cat)	<i>O</i> (%an)	<i>F</i> (%an)	
MnF ₂ -NaPO ₃ - ZnF ₂	28.6	14.3	28.6	28.6	50	50	Nominal
40 - 40 - 20	24.3	15.4	30.3	30.0	48.3	51.7	Analysed

Table 2

Characteristic temperatures and densities of 30 MnF₂ - 40 NaPO₃ -(30-x) LiF- x KF glasses. T_g for glass transition, T_x for onset of crystallization, T_p for exotherm maximum.

<i>Sample</i>	<i>x</i> (%)	<i>T_g</i> (± 2°C)	<i>T_x</i> (± 2°C)	<i>T_p</i> (± 1°C)	<i>T_x - T_g</i> (°C)	<i>Density</i> (g/cm ³)
MNLK0	0	200	247	258; 330	47	2.958
MNLK5	5	203	276	289; 331	73	2.942
MNLK10	10	212	321	328	109	2.930
MNLK15	15	211	335	340	124	2.919
MNLK 20	20	214	286	292	72	2.912
MNLK 25	25	213	274	280; 339	61	2.905
MNLK 30	30	233	287	295; 434	53	2.894

Table 3

Coefficient of thermal expansion of selected glasses.

<i>Glass Compositions</i>	<i>α ($10^{-7} K^{-1}$)</i>
05MnF ₂ -20ZnF ₂ -75NaPO ₃	188
15MnF ₂ -20ZnF ₂ -65NaPO ₃	189
25MnF ₂ -20ZnF ₂ -55NaPO ₃	189
30MnF ₂ -20ZnF ₂ -50NaPO ₃	185
35MnF ₂ -20ZnF ₂ -45NaPO ₃	188
40MnF ₂ -10ZnF ₂ -50NaPO ₃	188
20MnF ₂ -10ZnF ₂ -70NaPO ₃	183
40MnF ₂ -20KF-40NaPO ₃	210
20MnF ₂ -10SrF ₂ -70NaPO ₃	207
30MnF ₂ -20BaF ₂ -50NaPO ₃	226

Table 4

Young (*E*) and shear (*G*) modulus, Poisson ratio (*ν*) of fluorophosphate glasses in the x MnF₂-(80-x) NaPO₃-20 ZnF₂ system. Longitudinal *V_L* and transverse *V_T* velocities are obtained from ultrasonic measurements.

<i>MnF₂</i> (mol %)	<i>Density</i> (kg/m ³)	<i>V_L</i> (10 ³ m/s)	<i>V_T</i> (10 ³ m/s)	<i>E</i> (GPa)	<i>G</i> (GPa)	<i>ν</i>
0	2.783	4.32	2.34	39.3	15.2	0.290
05	2.812	4.48	2.47	43.8	17.2	0.275
15	2.929	4.92	2.57	50.2	19.3	0.301
20	2.999	4.59	2.60	51.6	20.2	0.276
25	3.059	4.88	2.62	53.4	21.0	0.272
30	3.109	4.80	2.68	56.9	22.3	0.273
35	3.205	5.10	2.63	58.4	22.2	0.317
40	3.264	4.86	2.69	60.0	23.5	0.275

Figures Captions

Fig. 1. Vitreous areas in ternary systems : MnF_2 - NaPO_3 - MF_n with $M = \text{Zn}$ (a), Sr (b), Ba(c), Mg (d), Na (e), Li (f) and K (g).

Fig. 2. DSC scans of 50MnF_2 - 50NaPO_3 (MNZ0) and 30MnF_2 - 50NaPO_3 - 20ZnF_2 (MNZ20) glasses. Heating rate: 10 K/min.

Fig. 3. Evolution of glass transition temperature T_g and thermal stability range T_x - T_g versus MnF_2 content: (a) $x \text{MnF}_2$ - $(80-x) \text{NaPO}_3$ - 20ZnF_2 and (b) $x \text{MnF}_2$ - $(90-x) \text{NaPO}_3$ - 10ZnF_2 .

Fig. 4. T_g and thermal stability range of the 30MnF_2 - 50NaPO_3 - 20MF_n glasses ($M = \text{Li, K, Mg, Sr, Zn and Ba.}$)

Fig. 5. Glass transition temperature T_g (a) and thermal stability range T_x - T_g (b) versus alkali content in 30MnF_2 - $(70-x) \text{NaPO}_3$ - $x \text{MF}$ glasses, with $M = \text{Li, Na and K.}$

Fig. 6. Evolution of density versus MnF_2 content. Glass composition :
(1) $x \text{MnF}_2$ - $(80-x) \text{NaPO}_3$ - 20ZnF_2 and (2) $x \text{MnF}_2$ - $(90-x) \text{NaPO}_3$ - 10ZnF_2

Fig. 7. Evolution of the Vickers microhardness versus MnF_2 concentration in the $x \text{MnF}_2$ - $(80-x) \text{NaPO}_3$ - 20ZnF_2 system. Line is drawn as a guide to the eye.

Fig. 8. Evolution of refractive index :
(a) vs MnF_2 concentration in $x \text{MnF}_2$ - $(80-x) \text{NaPO}_3$ - 20ZnF_2 system
(b) vs KF concentration in $30\% \text{MnF}_2$ - 40NaPO_3 - $(30-x) \text{LiF}$ - $x \text{KF}$ glasses

Fig. 9. UV-visible absorbance spectra of glasses in the $x\text{MnF}_2$ - 50NaPO_3 - $(50-x)\text{ZnF}_2$ system. Sample thickness: 2.4 mm.

Fig. 10. IR transmittance spectra of thin (1mm) and thick ($e=2.4\text{mm}$) samples of the MNZ20 glass: 30MnF_2 - 50NaPO_3 - 20ZnF_2 .

Fig. 11. IR transmittance spectra of 30MnF_2 - 50NaPO_3 - 20ZnF_2 glass
(a) between 400 and 1500 cm^{-1} , (powder dispersed in KBr)
(b) between 1000 and 4000 cm^{-1} (1mm-thick glass plate)

(a)

(b)

(c)

(d)

Fig. 1. Vitreous areas in ternary systems : MnF₂ - NaPO₃ - MFn with $M = \text{Zn}$ (a); Sr(b); Ba (c); Mg (d), Na (e); Li (f) and K (g).

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(a)

(b)

Fig. 5. Glass transition temperature T_g (a) and thermal stability range Tx-Tg (b) versus alkali content in 30MnF₂- (70-x)NaPO₃- x MF glasses, with $M = \text{Li, Na and K.}$

Fig. 6. Evolution of density versus MnF_2 content. Glass composition :
 (1) $x\text{MnF}_2 - (80-x)\text{NaPO}_3 - 20\text{ZnF}_2$ and (2) $x\text{MnF}_2 - (90-x)\text{NaPO}_3 - 10\text{ZnF}_2$

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