

Fluoride glasses of 3d transition metals

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Large vitreous areas have been found in PbF_2 - MF_2 - MF_3 systems ($M=3d$ transitional element). The chemical and thermal conditions of preparation are given. These glasses exhibit interesting physical properties: good infrared transparency up to $7.5 \mu m$ for 3 mm thickness, luminescence with rare earth ions, and spin glass behaviour for high Mn^{2+}/Fe^{3+} content. Furthermore, the octahedral coordination of 3d glass former ions gives a structural originality for these glasses as compared with fluoroberyllate or fluorozirconate glasses which are built on different coordinations.

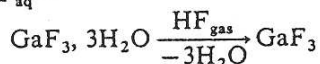
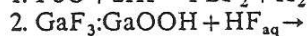
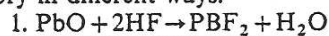
Previously fluoroberyllate glasses have been studied because of their structural analogy with silicate glasses.⁽¹⁻⁷⁾ The logical continuation of the work was the replacement of the inconvenient BeF_2 with MgF_2 ⁽⁸⁾ and recently studies on ZrF_4 , HfF_4 , or ThF_4 based fluoride glasses have shown a large diversity of glassy domains⁽⁹⁻¹²⁾ and the potential of these materials for infrared transmission.

In 1978 Miranday^(13,14) prepared a new family of fluoride glasses which differ from previous ones by the high content of 3d transition metal fluorides. The aim of this paper is to report on the properties of this class of fluoride glasses.

Experimental procedures

The handling of 3d transition element fluorides requires some precautions because of their sensitivity to hydrolysis by atmospheric water, which leads to the formation of oxides at temperatures higher than 300°C. Consequently, all operations (weighing, mixing, melting, and casting) were performed in dry boxes on line with an automated dryer unit.

The starting fluorides are prepared in the laboratory in different ways:



3. M_iF_2 and M_iF_3 (where M_i is a 3d transition element) were obtained from the action of HF_{gas} on anhydrous chlorides: the chlorides were obtained from commercial hydrated chlorides by dehydration under a dry ($N_2 + HCl$) stream.

The mixture of starting fluorides was placed in a covered platinum crucible and heated at between 600

and 900°C. The glass was cast on a preheated (200–250°C) bronze mould whose temperature was held for 30 min then cooled to room temperature at 200 degC/h.

Chemical studies

The first 3d transition metal glasses were found in the systems $MF-M_iF_2-M_iF_3$ with $MF=LiF, NaF, KF,$ or RbF ; $M_iF_2=PbF_2, CaF_2, SrF_2, CdF_2,$ or BaF_2 , and $M_iF_3=FeF_3, CrF_3, VF_3,$ or GaF_3 . Figure 1 shows the glassy domain in the $NaF-SrF_2-CrF_3$ system.

The second series of glasses were in the ternary systems $PbF_2-M_iF_2-M_iF_3$ with $M_iF_2=MnF_2, FeF_2, ZnF_2,$ or CuF_2 and $M_iF_3=FeF_3, CrF_3, VF_3, GaF_3,$ or InF_3 . The wide glassy domains (quenching at 20 degC) of $PbF_2-MnF_2-FeF_3$ and $PbF_2-MnF_2-InF_3$ systems are shown in Figure 2. The combination of good stability with promising infrared transparency led to more complete chemical investigations.^(15,16)

Many attempts to improve vitrification have been made, taking care to maintain the infrared transparency, by the addition or substitution of other fluorides have been made; Table 1 lists the best compositions obtained in the $PbF_2-MnF_2-FeF_3$ and $PbF_2-MnF_2-GaF_3$ systems together with their main physical characteristics. Figure 3 shows the variation of the infrared transparency of the 45PbF₂, 20MnF₂, 35FeF₃ glass with composition: the replacement of part of the PbF₂ by CaF₂ does not improve the vitrification and beyond 5% the transmission de-

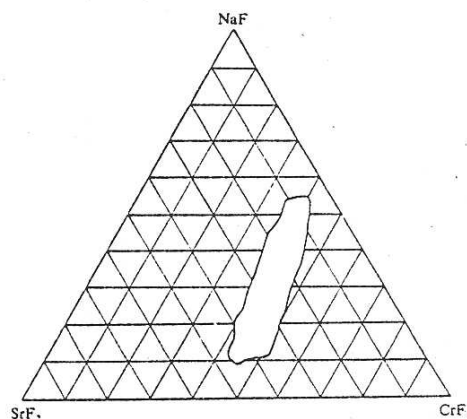
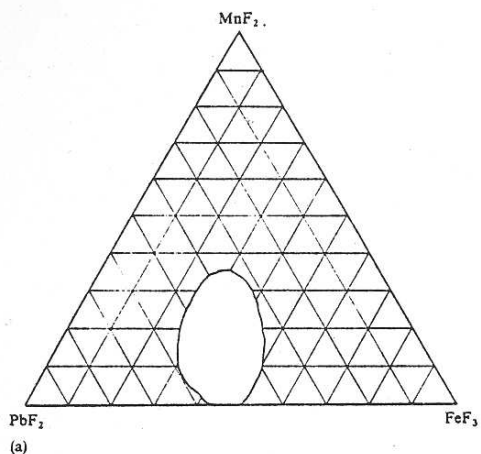
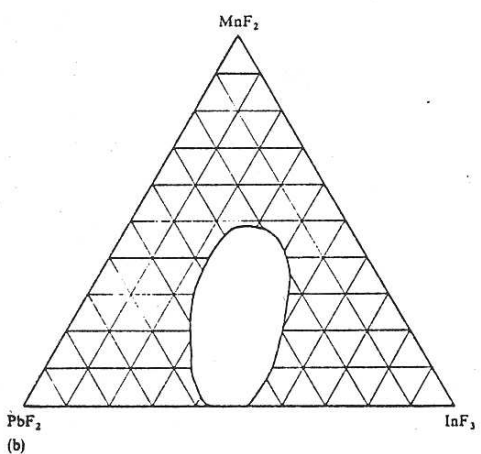


Figure 1. Area of glass formation in the $NaF-SrF_2-CrF_3$ system



(a)



(b)

Figure 2. Areas of glass formation in the PbF_2 - MnF_2 - FeF_3 (a) and PbF_2 - MnF_2 - InF_3 (b) systems

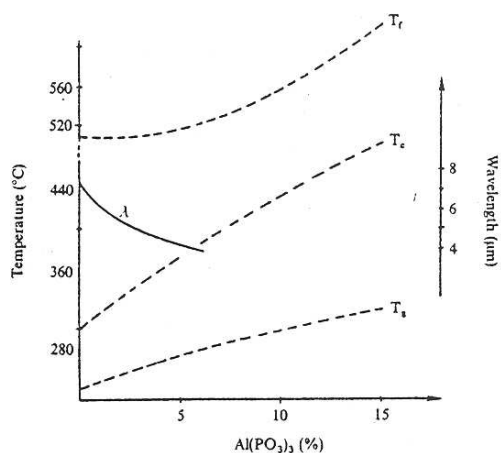
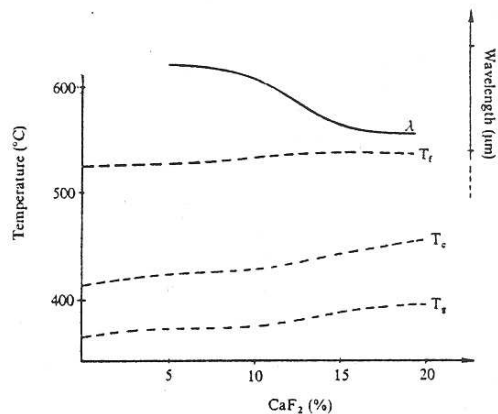


Figure 3. Variation of the infrared transmission threshold with concentration of additives in the $45PbF_2$, $20MnF_2$, $35FeF_3$ glass

Table 1. Compositions and properties of the glasses studied

| Composition | Size (mm) | Density ($g\ cm^{-3}$) | T_g ($^{\circ}C$) | T_c ($^{\circ}C$) | T_f ($^{\circ}C$) | Maximum transmittance for $\lambda > 2.5\ \mu m$ (%) | λ for $T > 50\%$ (μm) | n_D | v |
|--|-------------------------------|--------------------------|-----------------------|-----------------------|-----------------------|--|--------------------------------------|--------|-----|
| | | | | | | | | | |
| $45PbF_2, 20MnF_2, 35FeF_3$ (base composition) | $10 \times 10 \times 1$ | 6.0 | | | | | | 1.644 | 31 |
| $45PbF_2, 17MnF_2, 35FeF_3, 3CuF_2, 2AlF_3$ | $22.9 \times 14.4 \times 4$ | 5.9 | 243 | 304 | 525 | 70 | 7.3 | 1.643 | 31 |
| $45PbF_2, 17MnF_2, 30FeF_3, 3CuF_2, 5YF_3 + 2AlF_3$ | $38.5 \times 9.6 \times 8.1$ | 5.9 | 244 | 306 | 511 | 85 | 7.7 | 1.640 | 33 |
| $45PbF_2, 20MnF_2, 30FeF_3, 5YF_3, 2AlF_3$ | $37 \times 10.1 \times 7.8$ | 5.9 | 249 | 317 | 524 | 90 | 7.6 | 1.6395 | 31 |
| $40PbF_2, 20MnF_2, 35FeF_3, 5CaF_2 + 5AlF_3 + 2UF_4$ | $25.5 \times 21 \times 3.8$ | 5.5 | 285 | 390 | 497 | 50 | — | 1.6115 | 29 |
| $42PbF_2, 17MnF_2, 32FeF_3, 3SrF_2 + 5YF_3 + 2AlF_3$ | $37 \times 9.7 \times 8$ | 5.4 | 251 | 317 | 520 | 90 | 7.6 | 1.6275 | 34 |
| | $52 \times 18 \times 11.5$ | | | | | | | 1.6322 | 34 |
| $42PbF_2, 17MnF_2, 32FeF_3, 3SrF_2, 3CuF_2, 2InF_3, 1LaF_3 + 2AlF_3$ | $15.5 \times 10 \times 8.3$ | | 248 | 297 | 519 | 75 | 7.3 | 1.630 | 31 |
| $45PbF_2, 17MnF_2, 27FeF_3, 3CuF_2, 3CrF_3, 5YF_3 + 2AlF_3$ | $40 \times 8.2 \times 10$ | | 254 | 308 | 518 | 60 | 7.4 | 1.6445 | 33 |
| * $42PbF_2, 17MnF_2, 30FeF_3, 3SrF_2, 3CuF_2, 5YF_3 + 2AlF_3$ | $24 \times 12.5 \times 8.2$ | 5.5 | 253 | 310 | 523 | 90 | 7.7 | 1.6345 | 33 |
| $45PbF_2, 20MnF_2, 30FeF_3, 5GaF_3 + 5YF_3 + 2AlF_3$ | $40 \times 8 \times 8$ | 5.9 | 268 | 354 | 500 | 85 | 7.6 | 1.626 | 32 |
| $36PbF_2, 24MnF_2, 40GaF_3$ (base composition) | | | | | | | | | |
| $36PbF_2, 24MnF_2, 40GaF_3 + 2Al(PO_3)_3$ | $23.5 \times 14 \times 3.7$ | | 278 | 399 | 521 | 80 | 4.3 | | |
| $36PbF_2, 21MnF_2, 36GaF_3, 3CuF_2, 4YF_3 + 2ZrF_4$ | $20 \times 14.2 \times 3.3$ | 5.2 | 270 | 340 | 513 | 75 | 7.9 | 1.5785 | 43 |
| $36PbF_2, 22MnF_2, 36GaF_3, 2CoF_2, 4YF_3 + 2ZrF_4$ | $26 \times 14 \times 3.7$ | 5.2 | 270 | 339 | 527 | 85 | 7.7 | 1.5795 | 41 |
| $36PbF_2, 24MnF_2, 36GaF_3, 4YF_3 + 2ZrF_4$ | $18 \times 13.7 \times 4.8$ | | 263 | 341 | 515 | 85 | 7.9 | 1.5775 | 47 |
| $36PbF_2, 24MnF_2, 36GaF_3, 4YF_3 + 1 UF_4$ | $22 \times 13.6 \times 3.6$ | 5.3 | 272 | 349 | 521 | 85 | 7.9 | 1.5815 | 47 |
| † $36PbF_2, 24MnF_2, 35GaF_3, 5YF_3 + 2AlF_3$ | $22 \times 18 \times 7.8$ | 5.6 | 273 | 336 | 526 | 98 | 7.9 | 1.5767 | 40 |
| $36PbF_2, 24MnF_2, 33GaF_3, 7YF_3 + 2AlF_3$ | $21.9 \times 13.6 \times 3.3$ | 5.2 | 275 | 341 | 532 | 91 | 7.8 | 1.5877 | 43 |
| $34PbF_2, 22MnF_2, 35GaF_3, 2SrF_2, 2CuF_2, 5YF_3 + 2AlF_3$ | $24.6 \times 8 \times 8$ | 5.2 | 278 | 336 | 540 | 95 | 7.9 | 1.5730 | 41 |

*glass PMF20 (see Figure 5)
†glass PMG13 (see Figure 5)

creases; whereas the addition of $\text{Al}(\text{PO}_3)_3$ makes the vitrification easier but it dramatically affects the infrared transparency.

The vitrification of PMF and PMG glasses may be improved while still maintaining good infrared properties by the replacement of PbF_2 by 3–5% SrF_2 , the replacement of MnF_2 by 2–5% CuF_2 or ZnF_2 , or the addition of 3–10% YF_3 or 2–5% AlF_3 .

The limited solubility of ZrF_4 below a content of 10% in these glasses may indicate that the fluorozirconate glasses may be expected to have a different structure.

In the $\text{PbF}_2\text{-MF}_2\text{-MF}_3$ systems the best vitrification results are obtained in the order $\text{Mn}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ and $\text{Fe}^{3+} > \text{Ga}^{3+} > \text{V}^{3+}$; the use of Co^{2+} , Ni^{2+} , and Cr^{3+} often leads to partially crystallised materials ('vitrocerams').

Characterisation of the glasses

The glasses are resistant to atmospheric moisture and may be kept at up to 200°C in air without damage. Their resistance to an aqueous solution depends on the pH, the attack being greater in an acidic medium. Other general physical properties of these glasses include a thermal expansion comparable to that of fluorozirconates ($\approx 15 \times 10^{-6}$) and a low hardness ($200 < H_{V100} < 300$).

For some compositions, an excellent coating on pure or alloyed aluminium or copper is possible if the temperature of the metallic substrate is held 20 degC above the transition temperature. The adherence on iron or steel is very dependent upon the surface state.

The samples may be polished by abrasion on dry or oiled surfaces and cleaned by trichlorethylene or chloroform.

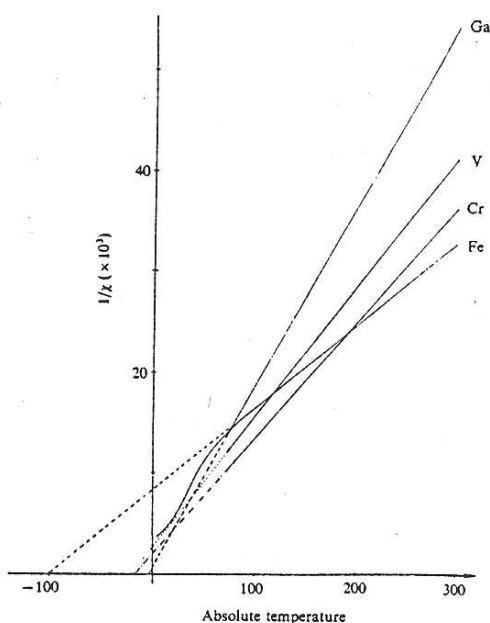


Figure 4. Variation of magnetic susceptibility with temperature for $\text{Pb}_2\text{MnM}^{\text{III}}\text{F}_9$ glasses

Magnetic properties

Magnetic studies on 3d transition metal fluoride glasses corroborate the predominance of superexchange antiferromagnetic interactions. Figure 4 shows the magnetic susceptibility of $2\text{PbF-MnF}_2\text{-MF}_3$ glasses with $\text{M}^{\text{III}} = \text{V}^{3+}$, Cr^{3+} , Fe^{3+} , or Ga^{3+} . Table 2 gives the Curie temperature and it can be shown that for $d^3\text{-}d^5$ ($\text{Mn}^{2+}\text{-Fe}^{3+}$) the first neighbour interactions are strongly antiferromagnetic.

Magnetic vitreous insulators with predominant superexchange antiferromagnetic interactions are frustrated systems because of their topological disorder. They may have a spin glass transition at low temperature. In the case of the $\text{PbF}_2\text{-MnF}_2\text{-FeF}_3$ and $2\text{PbF}_2\text{-MnF}_2\text{-FeF}_3$ glasses, such a transition has been found by ac susceptibility measurements at 11.77 and 5.26 K respectively. Extensive studies have been performed on these glasses.⁽¹⁷⁻²⁰⁾

Table 2. Curie temperatures of some of the glasses studied

| Glass | Curie temperature (K) |
|-----------------------------|-----------------------|
| PbMnFeF_7 | -190 |
| PbCuFeF_7 | -130 |
| $\text{Pb}_2\text{MnFeF}_9$ | -100 |
| $\text{Pb}_2\text{MnCrF}_9$ | -20 |
| Pb_2MnVF_9 | -20 |
| $\text{Pb}_2\text{MnGaF}_9$ | -10 |

Optical properties

Ultraviolet and visible

Except for Mn in MnCrF_5 ⁽²¹⁾ the 3d transition metals in crystalline fluorides are always in octahedral coordination. The absorption spectra of glasses based on Ni^{2+} , Co^{2+} , Cr^{3+} , or V^{3+} show complete analogy with those of crystalline compounds⁽¹⁴⁾ and as the crystallochemical behaviour of Mn^{2+} , Cu^{2+} , Zn^{2+} , Fe^{3+} , and Ga^{3+} ions is similar to that of the above ions, we can consider our glasses as being composed of M_6F_6 octahedra linked together. Because of the charge transfer phenomenon for glasses based on Fe^{3+} and Ga^{3+} , the latter are more suitable for the visible region, but close to 0.28 μm there is a large absorption peak due to Pb^{2+} which closes the transparency window towards the ultraviolet.

Luminescence

These glasses are the first examples in fluorine chemistry of the coexistence of large amounts of 3d and 4f ions; this is of interest first for magnetism and second for optics because of their very low absorption in the far infrared (giving hopes of making optical fibres with weak Rayleigh scattering) together with low vibrational frequencies (which are a major condition for low multiphonon deexcitation, competing with luminescence). Luminescence studies were therefore under-

taken on Er^{3+} in the $\text{PbF}_2\text{-(Mn, Zn)F}_2\text{-GaF}_3$ glasses⁽²²⁾ and $\text{Mn}^{2+}\text{-Er}^{3+}$ energy transfer was found for the manganese glass.

Infrared transparency

Very good transparency is maintained down to 7.5 μm in all the glasses studied up to a thickness of 3 mm (Figure 5) and hence these materials, specially the PMG glasses, are potential candidates for 2–6 μm windows. Tests on the possibility of making fibres are in progress.

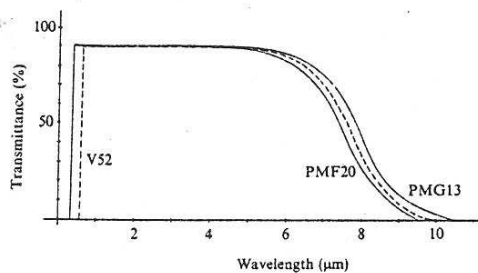


Figure 5. Infrared window of PMF 20 and PMG 13 glasses (Table 1) compared to that of fluorozirconate glass V52⁽²³⁾

Structural considerations

Visible and ultraviolet absorption spectra unambiguously show that the 3d transition network forming ions are in octahedral coordination. Thus the structure of these glasses differs from that of fluorozirconate glasses in which the average coordination seems to be higher. The crystallochemical problem, therefore, is to account for a metastable vitreous state by the means of regular octahedral connections. The results of ^{19}F NMR on $2\text{PbF}_2\text{-MnF}_2\text{-FeF}_3$ glass with diamagnetic ion substitutions ($\text{Mn}^{2+}/\text{Zn}^{2+}$ and $\text{Fe}^{3+}/\text{Ga}^{3+}$) are consistent with a corner-shared octahedral

chain model with no Mn–Mn or Fe–Fe pairs.⁽¹⁹⁾ This kind of reticulation agrees well, for average paramagnetic ion distances, with preliminary results from neutron diffraction experiments.⁽²⁴⁾

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References

1. Goldschmidt, V. M. (1926). *Skr. norske Vidensk.-Akad. Mat.-naturv. Kl.* 8, 7.
2. Roy, D. M., Roy, R. & Osborn, E. F. (1950). *J. Am. Ceram. Soc.* 36, 185.
3. Imaoka, M. & Mizusawa, S. (1953). *J. Ceram. Ass. Japan* 61, 13.
4. Heyne, G. (1933). *Angew. Chem.* 46, 473.
5. Vogel, W. & Gerth, K. (1958). *Glastech. Ber.* 31, 15.
6. Izumitani, T. & Terai, R. (1952). *Bull. Osaka Ind. Res. Inst.* 3, 25.
7. Sun, K. H. & Callear, T. (1949). *USP* 2 466 506.
8. Sun, K. H. (1949). *USP* 2 466 509.
9. Poulain, M., Poulain, M., Lucas, J. & Brun, P. (1975). *Mater. Res. Bull.* 10, 243.
10. Poulain, M., Chantanasingh, M. & Lucas, J. (1977). *Mater. Res. Bull.* 12, 151.
11. Drexhage, M. G., Moynihan, C. T. & Saleh, M. (1980). *Mater. Res. Bull.* 15, 213.
12. Guery, J., Courbion, C., Jacoboni, C. & De Pape, R. To be published in *Mater. Chem.*
13. Miranday, J. P., Jacoboni, C. & De Pape, R. (1979). *Rev. Chim. minér.* 16, 277.
14. Miranday, J. P., Jacoboni, C. & De Pape, R. (1981). *J. Non-Cryst. Solids* 43, 393.
15. Brevet ANVAR-CNRS Serie 23 no. 79-07785.
16. Contrat DRET, Division Optique (80/1045).
17. Renard, J. P., Miranday, J. P. & Varret, F. (1980). *Solid St. Commun.* 35, 41.
18. Velu, E., Renard, J. P. & Miranday, J. P. (1981). *J. Physique* 42, 237.
19. Dupas, C., Le Dang, K., Renard, J. P., Veillet, P., Miranday, J. P. & Jacoboni, C. (1981). *J. Physique* 42, 1345.
20. Renard, J. P., Dupas, C., Velu, E., Jacoboni, C., Fonteneau, G. & Lucas, J. (1981). *Physica B* 108, 1291.
21. Ferey, G., De Pape, R., Poulain, M., Grandjean, D. & Hardy, A. (1976). *Acta crystallogr.* B33, 1409.
22. Reisfeld, R., Katz, G., Spector, N., Jørgensen, C. K., Jacoboni, C. & De Pape, R. (1982). *J. Solid St. Chem.* 41, 253.
23. Poulain, M. & Lucas, J. (1978). *Verres Réfract.* 32 (4), 505.
24. Le Bail, A., Courbion, G., Jacoboni, C. & De Pape, R. Accepted for publication in *J. Solid St. Chem.*