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## RAMAN SPECTROSCOPY OF FLUORIDE GLASSES

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There has been considerable research activity recently in the preparation and characterization of multicomponent glasses based on heavy metal fluorides which offer excellent prospects for multispectral transmission (from .2 to 8  $\mu\text{m}$ ) with ultra low loss near 2.5  $\mu\text{m}$  (theoretically  $10^{-3}$  dB/km and experimentally about .7 dB/km on a fiber of 60 m length [1]). 3d transition metal fluoride glasses (TMFG, [2,3]) have basically the same properties.

Numerous structural studies with various methods (X-ray and nuclear diffraction [4, 5], E.X.A.F.S. [6, 7], simulation [8]) have been performed to obtain information on the short and medium range orders.  $\text{MF}_6$  are the basic structural units of TMFG structure ; they are predominantly linked by corners and the results of modelling show that locally the organization is not far from that of crystallized phases with close composition. Close packing between  $\text{F}^-$  and large cations ( $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ) induced by the vicinity of their ionic radii, with transition metal ( $\text{Mn}^{2+}$ ,  $\text{Ga}^{3+}$ ) in octahedral holes, may be the structural common denominator of TMFG. They could be also described by an octahedral random network with large cations in interstitial sites.

Basically, all fluoride glasses give the same Raman spectrum profile [9] with a main line in the 500-600  $\text{cm}^{-1}$  range which is commonly attributed to the vibration of the metal-fluorine bond [10, 11]; the present study is devoted to the variation of this line with the nature of the cation, assuming isostructural behaviour of the substitution cation.

Experimental procedure. The RAMAN study is performed with an Argon laser (Innova 90) at ambient temperature on a DILOR Z24 spectrophotometer with triple monochromator using photon detection.

Polished glass samples of about 15x5x5  $\text{mm}^3$  have been prepared [3] :

PMG 36  $\text{PbF}_2$  24  $\text{MnF}_2$  35  $\text{GaF}_3$  5  $\text{YF}_3$  2  $\text{AlF}_3$

PZG 36  $\text{PbF}_2$  24  $\text{ZnF}_2$  35  $\text{GaF}_3$  5  $\text{YF}_3$  2  $\text{AlF}_3$

PBI 19  $\text{PbF}_2$  23  $\text{BaF}_2$  5  $\text{SrF}_2$  47  $\text{InF}_3$  5  $\text{ZnF}_2$  2  $\text{AlF}_3$

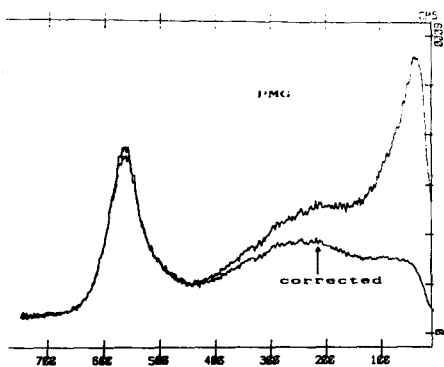


Fig. 1

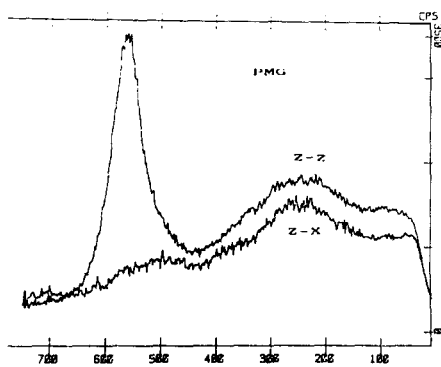


Fig. 2

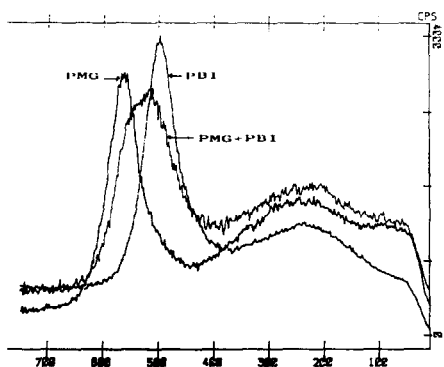


Fig. 3

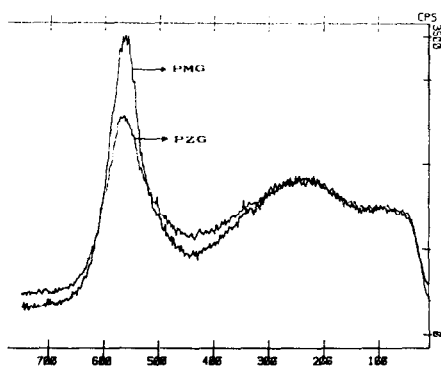


Fig. 4

**Results.** Fig. 1 shows the influence of Bose-Einstein correction at low frequency. The  $600\text{ cm}^{-1}$  RAMAN line is Z Z polarized (Fig.2); this line is compatible with fluoride ions bonded to a octahedrally coordinated metal as in  $\text{KAlF}_4$  (Fig.3. [12]). The structural analogy between  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  ions ( $\langle\text{M-F}\rangle$  distances are respectively  $1.96\text{ \AA}$  and  $1.93\text{ \AA}$  [7]) is confirmed in Fig.4 which shows the spectra of PMG and PZG. In the classical sense of glass makers, 3d transition metals are network formers; assuming roughly full structural behaviour analogy (distances and coordination number) for  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{In}^{3+}$  and  $\text{Al}^{3+}$ , the shift of the  $565\text{ cm}^{-1}$  line can be related to the variation of  $\langle\text{M-F}\rangle$  bond length (from  $1.98\text{ \AA}$  for PMG to  $2.08$  for PBI). In fact, the coordination number for  $\text{In}^{3+}$  could be higher than 6 in this glass as it can be 7 in many cases in the crystallized fluorides.

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