1123

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ENHANCED OPTICAL PROPERTIES OF Tm^{3+} IN F CO-DOPED LEAD GERMANATE GLASSES FOR FIBER DEVICE APPLICATIONS

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The effect on structure and property of adding fluoride into Tm^{3+} doped lead-germanate glass was established and verified experimentally. It was found that up to 10 mol% of fluoride could be introduced into our original lead-germanate composition while retaining the high thermal stability ideal for fibre fabrication. Much improved spectroscopic features, namely increased fluorescent lifetimes from $^3H_4$ and $^3F_4$ levels in Tm^{3+} with increasing fluorine content, were observed. At the same time it was found that the radiative properties of Tm^{3+} were left unchanged by fluoride addition, indicating that reduced multiphonon relaxation was responsible for the increased fluorescent lifetimes. This was well explained and foreseen by our established structure-property relation in terms of adding fluorine to the glass. In conclusion, fluoro-germanate glass shows advantages over germanate glass in optical properties and over fluoride glass in chemical and mechanical properties for practical fiber device applications.

1123

Enhanced Optical Properties of Tm^{3+} In F Co-Doped Lead Germanate Glasses For Fibre Device Application

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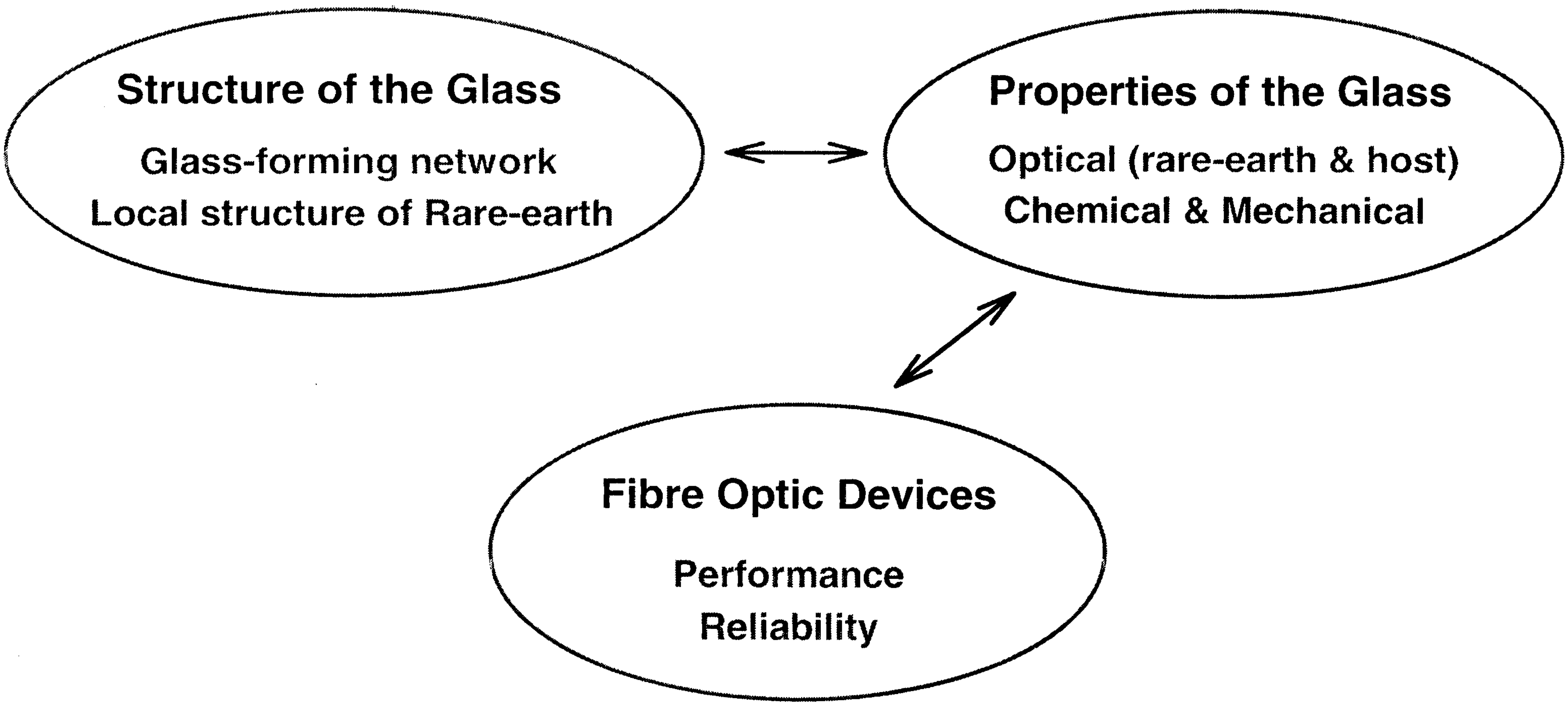
INTRODUCTION



GLASS FABRICATION

Thermally stable composition:

$55GeO_2$-$20PbO$-$10BaO$-$10ZnO$-$5K_2O$

J. Wang et al., J. Appl. Phy., 73(12) (1993) 8066.

Fluoride Introduction:

PbF_2 -----> PbO

BaF_2 -----> BaO

ZnF_2 -----> ZnO

Active element: Tm_2O_3

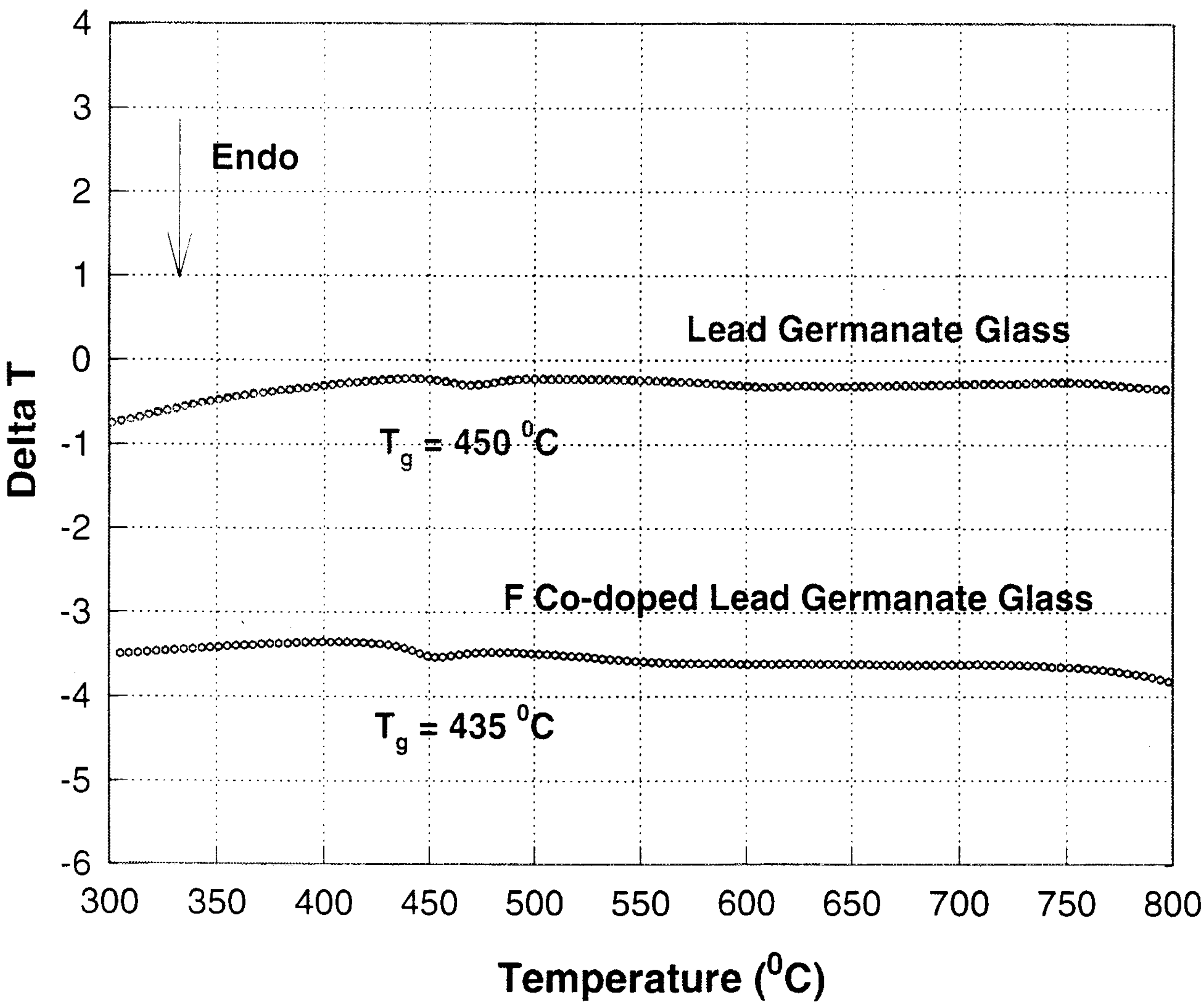
Processing condition:

Melting temperature: 1100 - 1150 ^0C

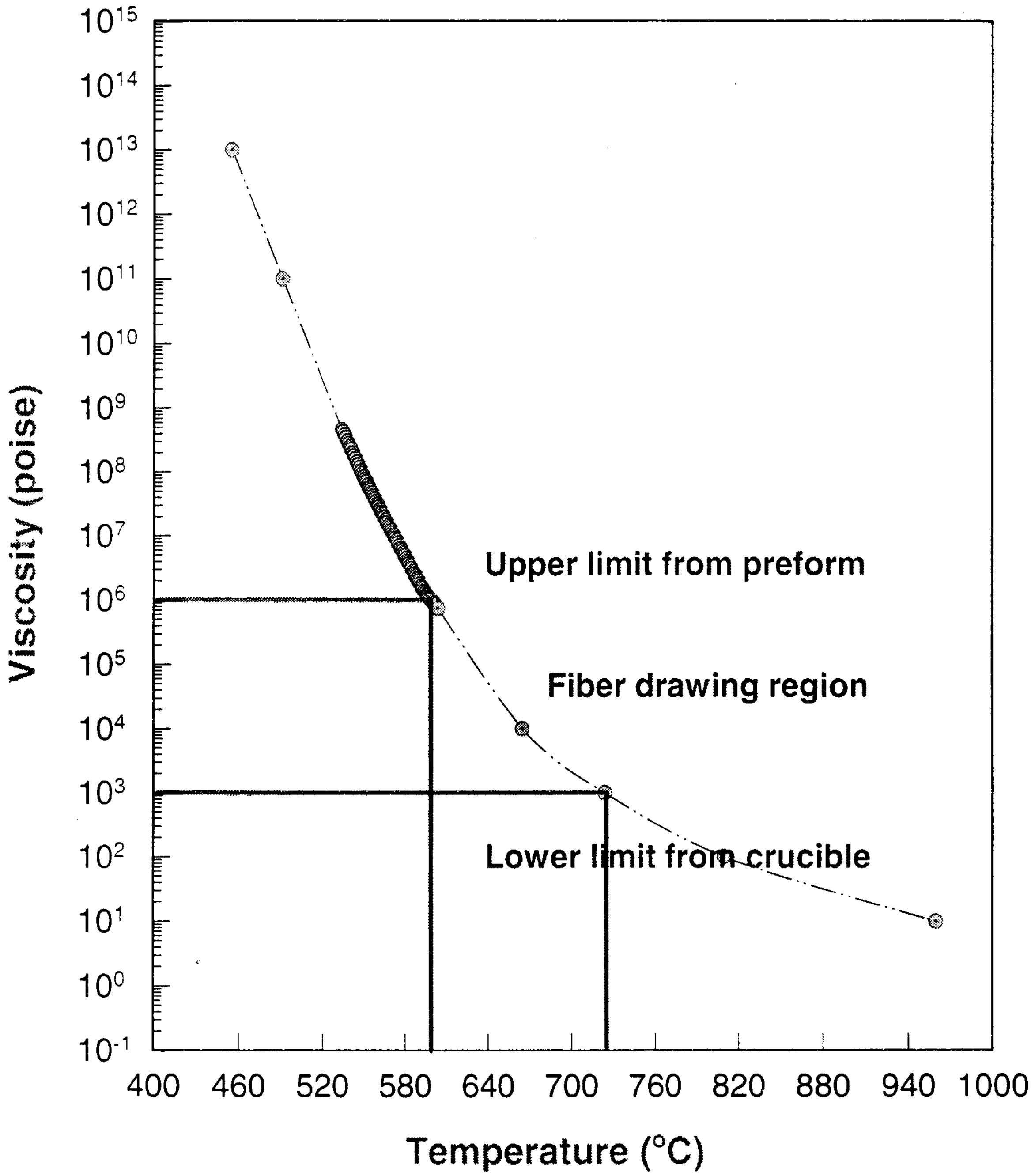
Annealing temperature: 400 - 450 ^0C

Thermal Properties of the Glasses

The thermal stability after F co-doing is well kept in all glasses with fluoride concentration up to 10 mol% measured by Differential Thermal Analysis.

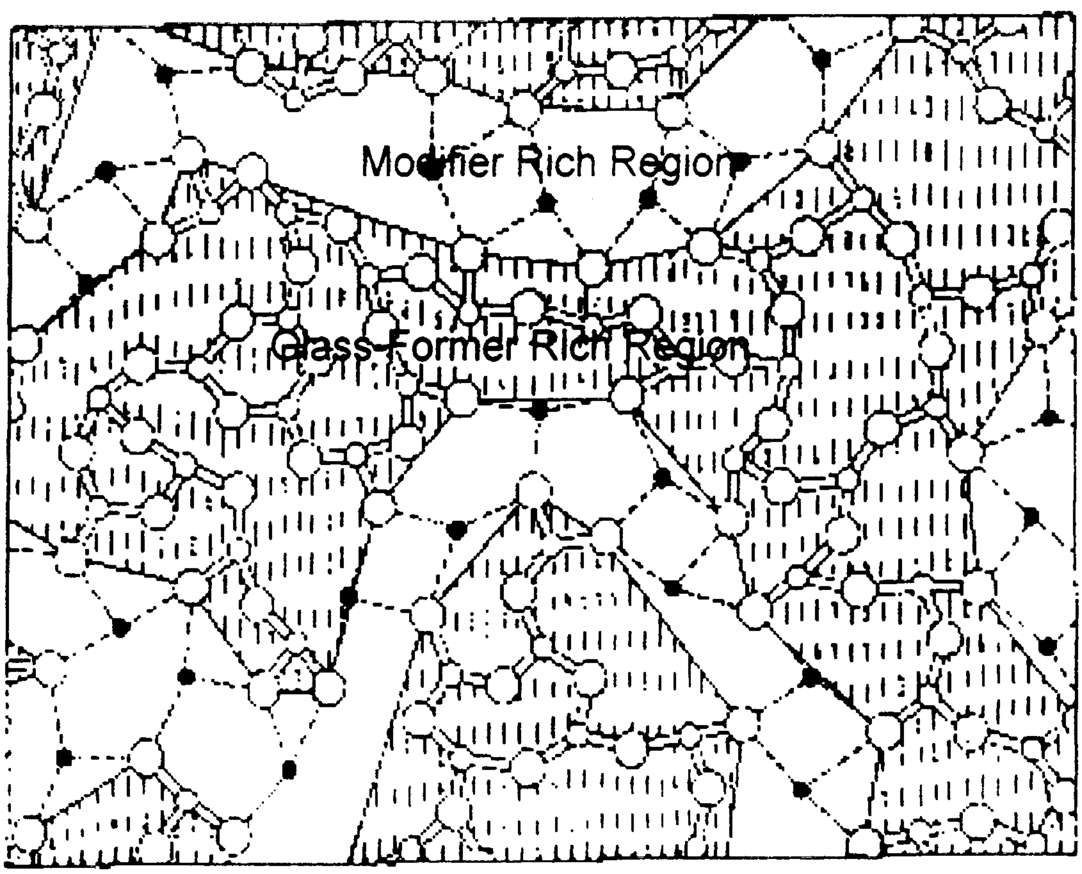


Viscosity of lead germanate glass

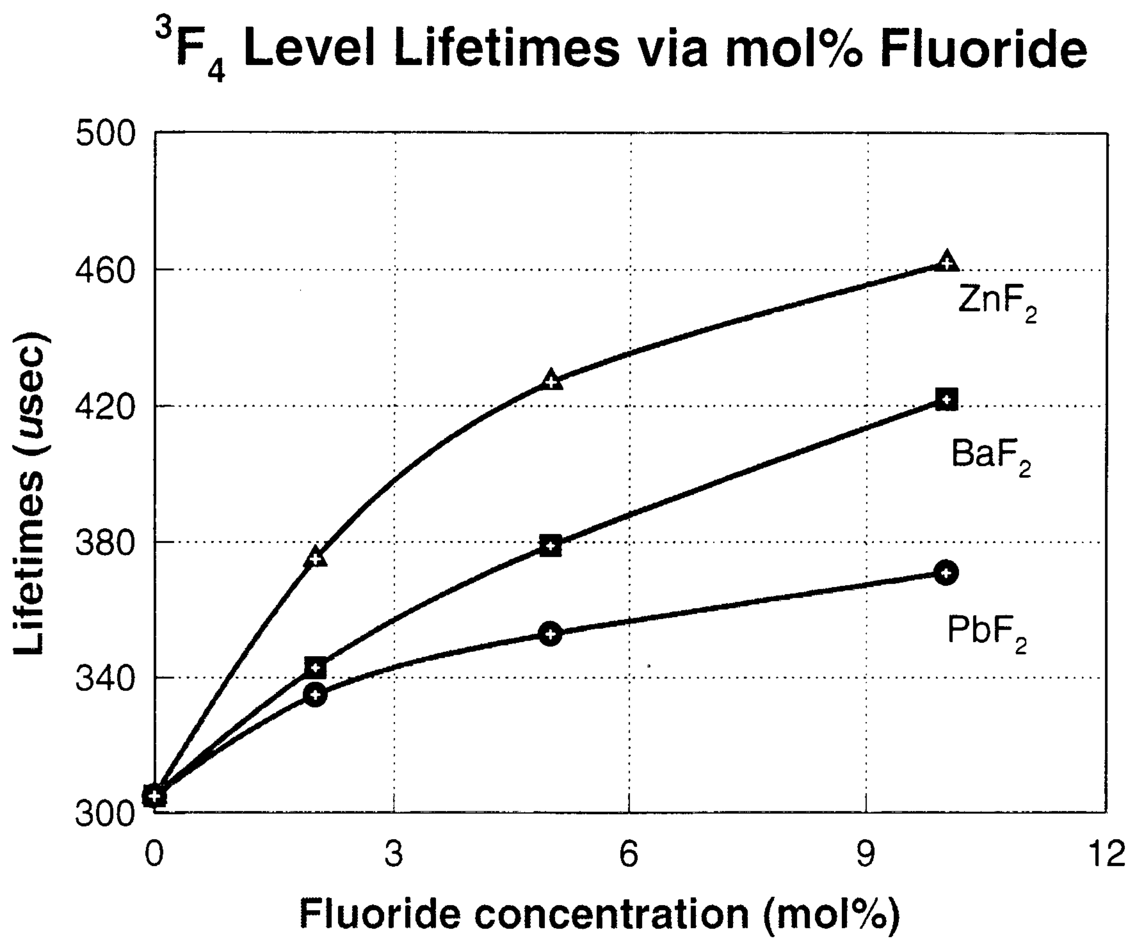


Local Structure of Tm^{3+} Ions

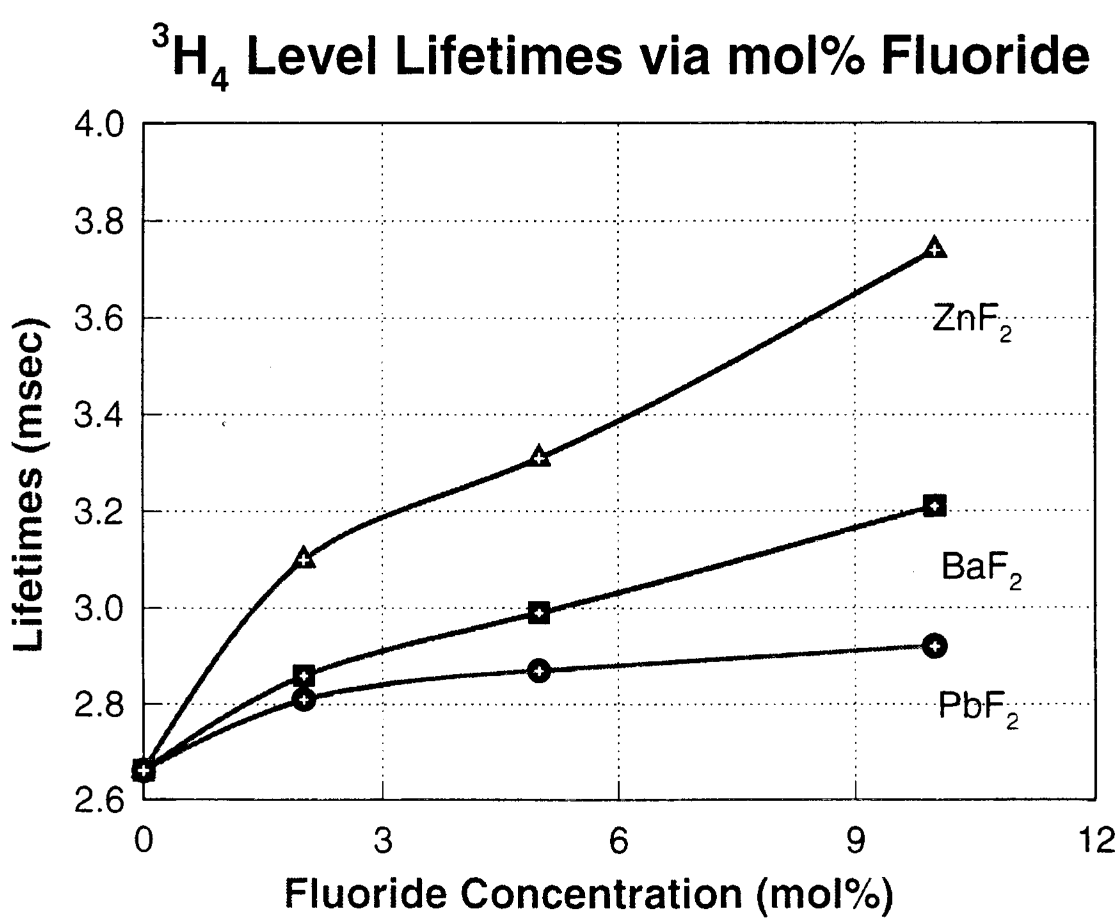
Based on '*modified random network*' model in glass structure (see the figure below) and using '*crystal chemistry principles*'[1], it is suggested that the Tm^{3+} will be at a F rich environment with F both in the modifier-rich region of the glass.



1. J. Wang, W.S. Brocklesby et al., J. Non-cryst. Solids, 163 (1993) 261.



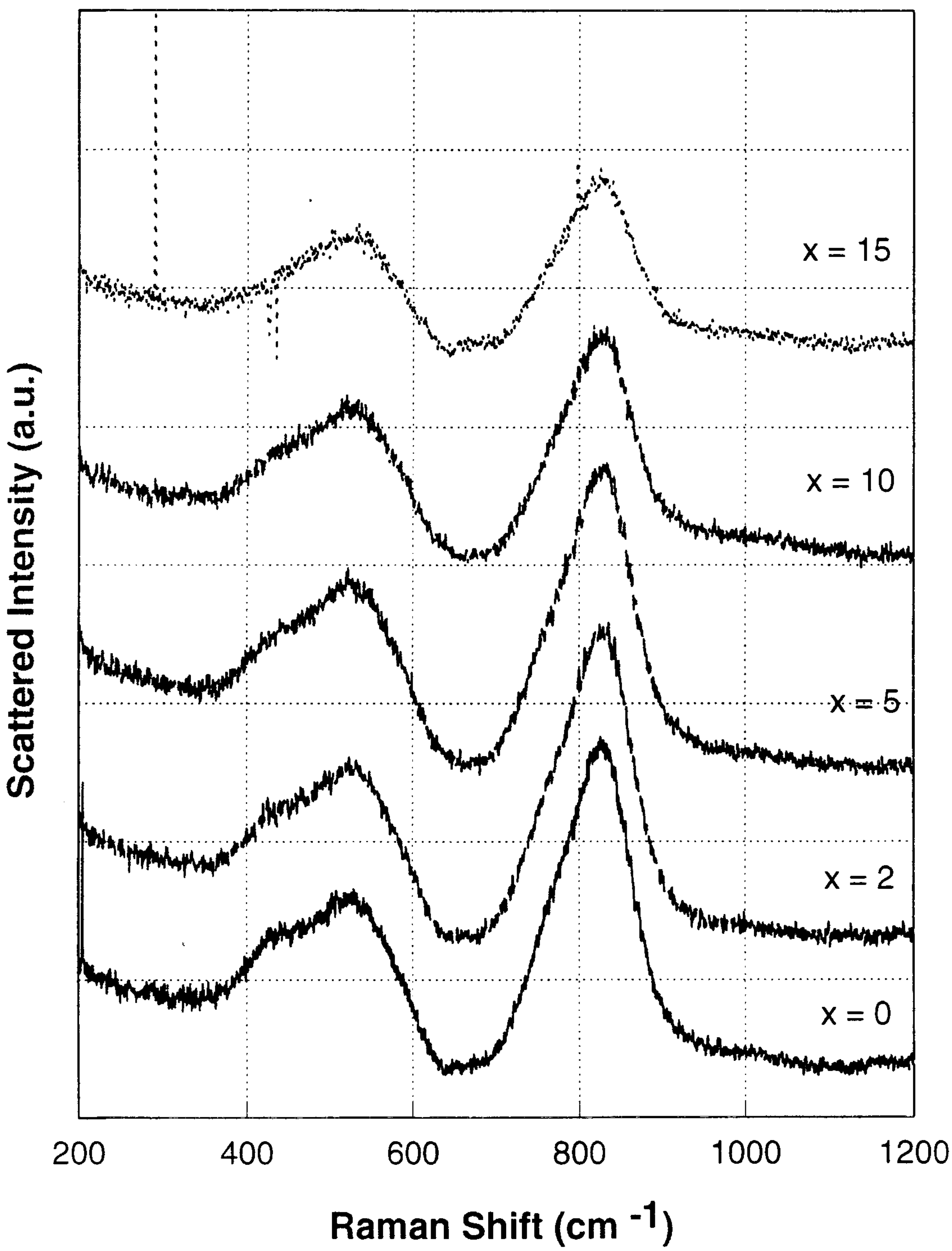
$^3F_4$ Level Lifetimes via mol% Fluoride
500
460
420
380
340
300
Lifetimes (usec)
0
3
6
9
12
Fluoride concentration (mol%)
ZnF_2
BaF_2
PbF_2



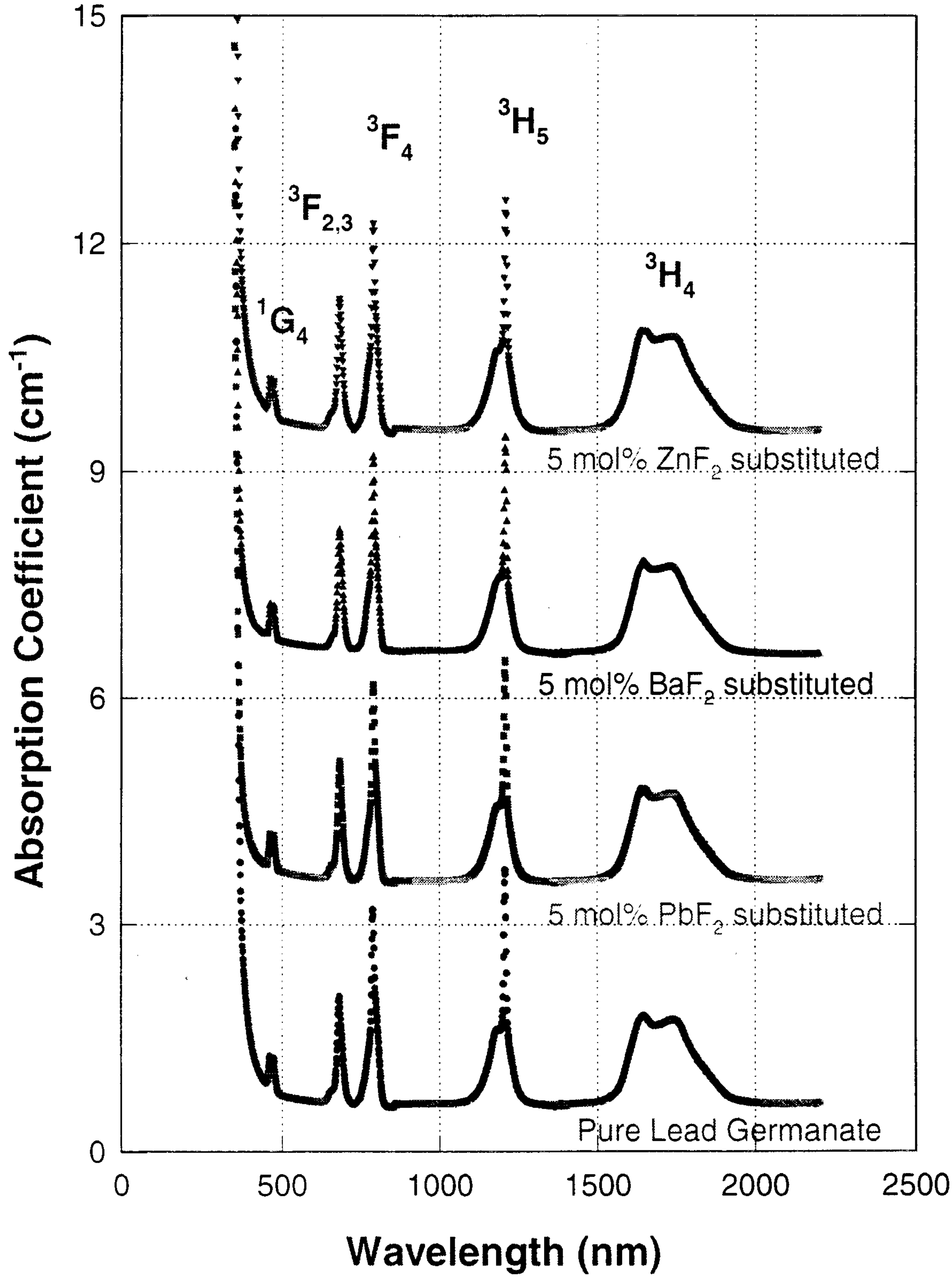
$^3H_4$ Level Lifetimes via mol% Fluoride
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
Lifetimes (msec)
0
3
6
9
12
Fluoride Concentration (mol%)
ZnF_2
BaF_2
PbF_2

Raman Spectra of Glasses in the System of

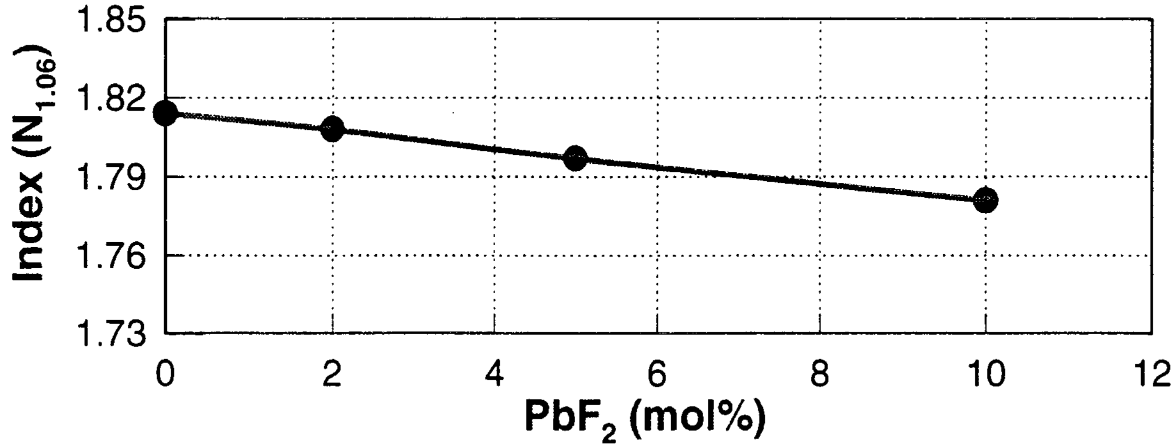
$55GeO_2(20\text{-}X)PbOXPbF_2 10ZnO10BaO5K_2O$

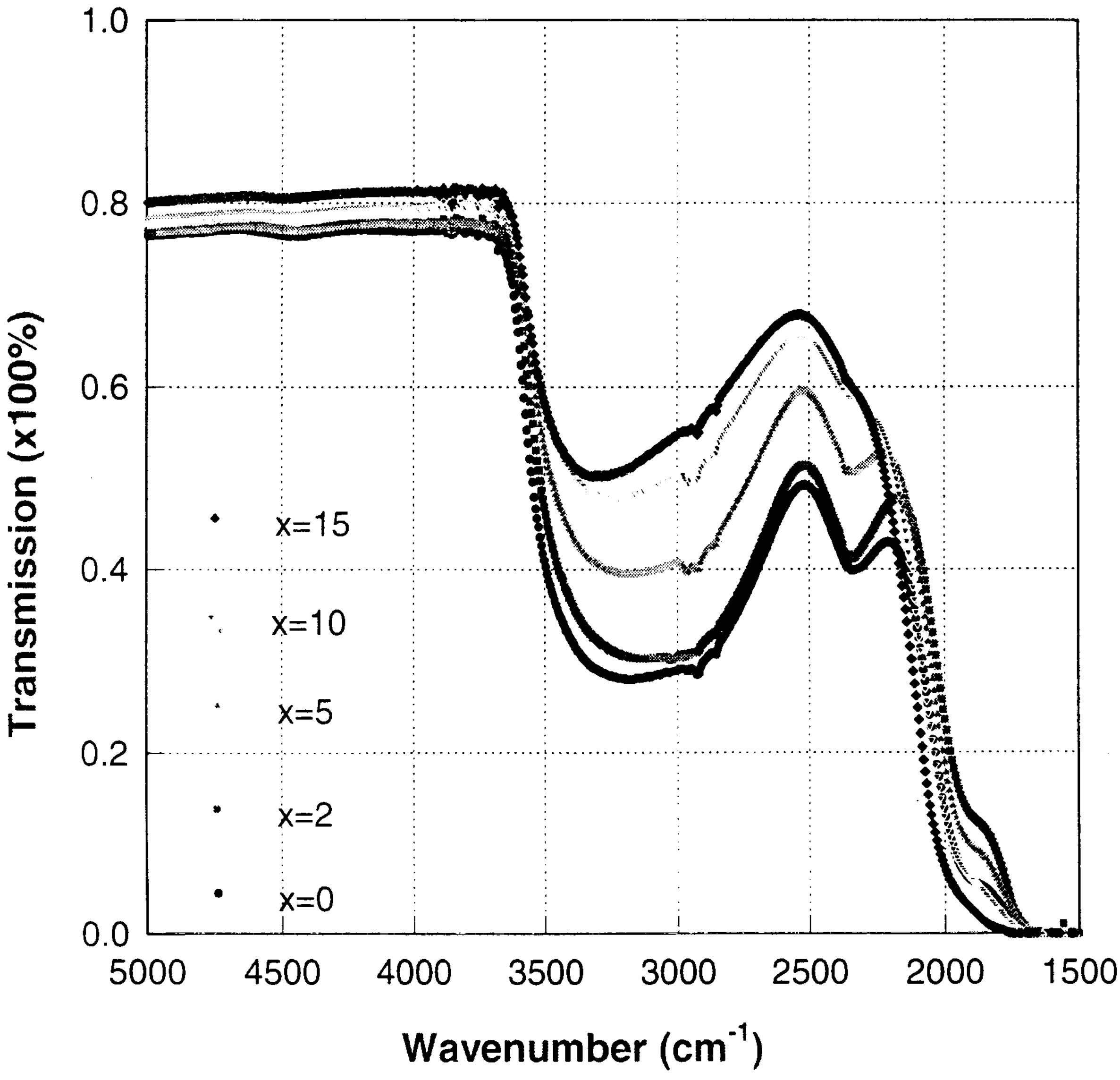


Absorption Spectra of Tm^{3+}



Refractive Indices and FTIR Spectra of Glasses in $55GeO_2(20\text{-}X)PbOXPbF_210ZnO10BaO5K_2O$ System





Non-radiative Multiphonon Relaxation Rate

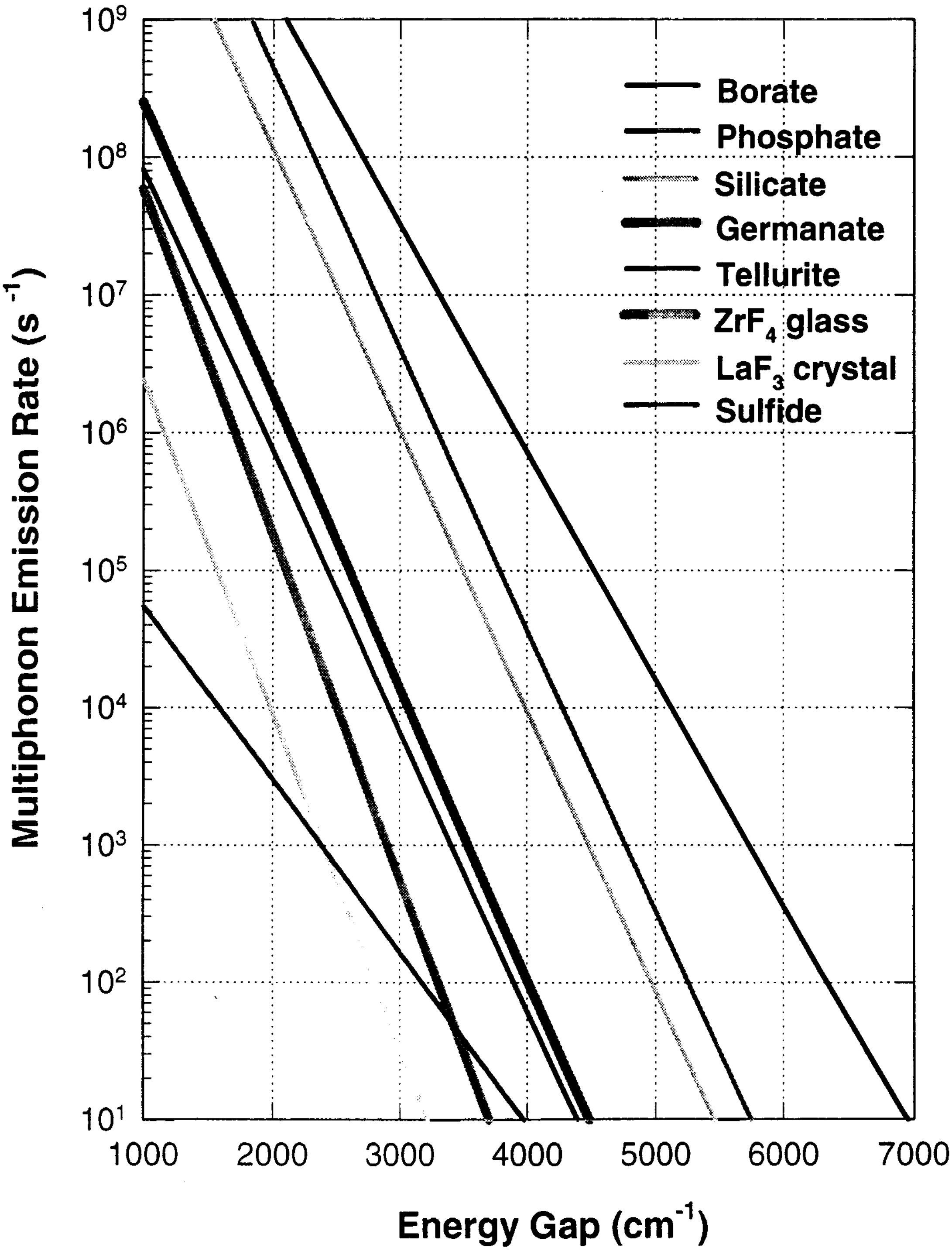
$$W_{nr} = C \cdot \exp(-\alpha \cdot \Delta E)$$

and $$\alpha = -\ln(\epsilon)/\hbar\omega$$

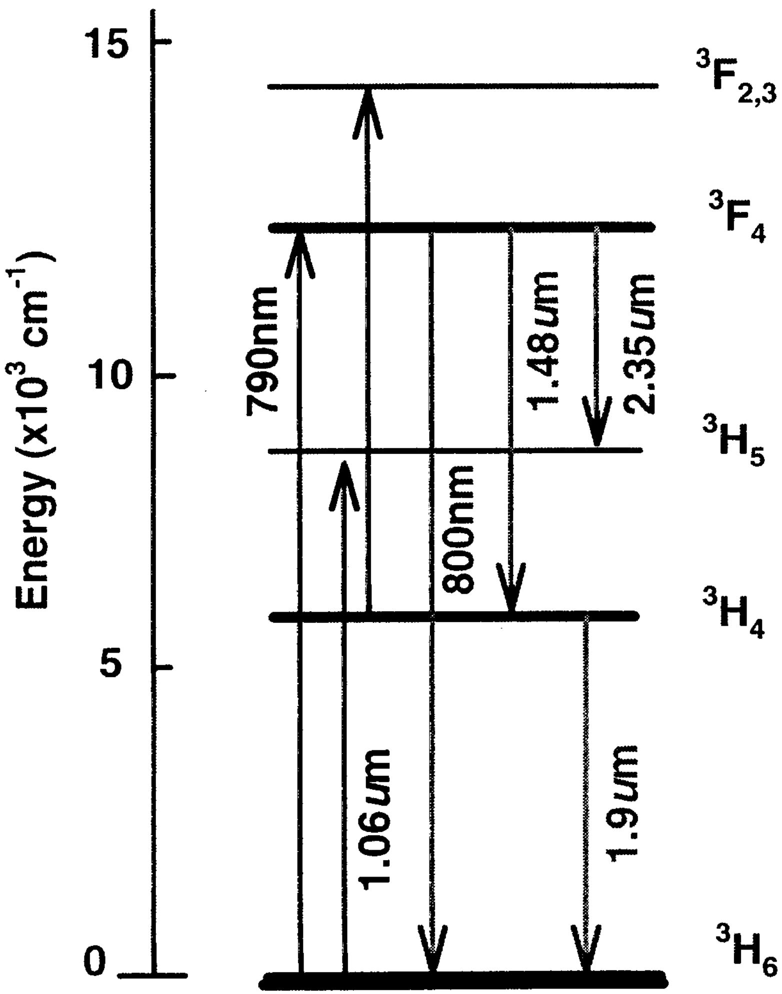
Stronger electron-phonon coupling ⇔ Smaller α

Host	**C (s^{-1})**	**α (10^{-3} cm)**	**ħω (cm^{-1})**
Borate	2.9×10^{12}	3.8	1400
Phosphate	5.4×10^{12}	4.7	1200
Silicate	1.4×10^{12}	4.7	1100
Germanate	**3.4×10^{10}**	**4.9**	**900**
Tellurite	6.3×10^{10}	4.7	700
Fluorozirconate	**1.59×10^{10}**	**5.77**	**500**
LaF_3 (cryst)	6.6×10^{8}	5.6	350
Sulfide	10^{6}	2.9	350

Multiphonon Emission Rate Via Energy Gap



Energy Levels of Tm^{3+} Ion



RESULTS SUMMARY

1. Radiative Properties

After co-doping F, radiative property of the glasses maintains virtually the *same* as the pure lead-germanate glass.

2. Non-Radiative Properties

F co-doping induces *lower* multiphonon relaxation rate due to *reduced phonon-electron coupling* strength although the maximun phonon-energy stays the same.

3. Quantum Yield

Radiative quantum yield from the meta-stable $^3F_4$ and $^3H_4$ levels *increases* as F is introduced.

CONCLUSION

1. Successfully introduced F into lead-germanate glass while retaining the thermal stability ideal for fibre fabrication.

2. Established structure-property relationship in terms of adding F and confirmed with experimental results.

3. Fluoro-germanate glass has advantages over germanate in optical properties and over fluoride in chemical and mechanical properti-es in practical fibre device applications.