ENHANCED OPTICAL PROPERTIES OF Tm$^{3+}$ IN F CO-DOPED LEAD GERMANATE GLASSES FOR FIBER DEVICE APPLICATIONS
J. WANG, J. HECTOR$^1$, W.S. BROCKLESBY, D.J. BRINCK AND D.N. PAYNE, OPTOELECTRONICS RESEARCH CENTRE AND DEPT. OF PHYSICS$^1$, THE UNIVERSITY, SOUTHAMPTON SO17 1BJ, UK

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

J. Wang, J.H. Hector$^1$, W.S. Brocklesby,
D.J. Brinck and D.N. Payne

Optoelectronics Research Centre and Department of Physics$^1$
The University, Southampton SO17 1BJ, England
INTRODUCTION

Structure of the Glass
- Glass-forming network
- Local structure of Rare-earth

Properties of the Glass
- Optical (rare-earth & host)
- Chemical & Mechanical

Fibre Optic Devices
- Performance
- Reliability
GLASS FABRICATION

Thermally stable composition:

\[ 55\text{GeO}_2 - 20\text{PbO} - 10\text{BaO} - 10\text{ZnO} - 5\text{K}_2\text{O} \]


Fluoride Introduction:

\[ \text{PbF}_2 \rightarrow \text{PbO} \]
\[ \text{BaF}_2 \rightarrow \text{BaO} \]
\[ \text{ZnF}_2 \rightarrow \text{ZnO} \]

Active element: \( \text{Tm}_2\text{O}_3 \)

Processing condition:

Melting temperature: \( 1100 - 1150 \, ^\circ\text{C} \)
Annealing temperature: \( 400 - 450 \, ^\circ\text{C} \)
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*’, 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.

Raman Spectra of Glasses in the System of

55GeO₂(20-X)PbOXPbF₂10ZnO10BaO5K₂O

Scattered Intensity (a.u.)

Raman Shift (cm⁻¹)
Absorption Spectra of Tm³⁺

Absorption Coefficient (cm⁻¹)

Wavelength (nm)
Refractive Indices and FTIR Spectra of Glasses in 
$55\text{GeO}_2(20-X)\text{PbOX}\text{PbF}_2\text{10ZnO10BaO5K}_2\text{O}$ System

![Graph of refractive index (N_{1.06}) vs. PbF$_2$ (mol%)](image1)

![Graph of transmission (x100%) vs. wavenumber (cm$^{-1}$)](image2)
Non-radiative Multiphonon Relaxation Rate

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

and \[ \alpha = -\ln(\varepsilon) / \hbar \omega \]

Stronger electron-phonon coupling ⇔ Smaller \( \alpha \)

<table>
<thead>
<tr>
<th>Host</th>
<th>( C ) ( (s^{-1}) )</th>
<th>( \alpha ) ( (10^{-3} \text{ cm}) )</th>
<th>( \hbar \omega ) ( (\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borate</td>
<td>( 2.9 \times 10^{12} )</td>
<td>3.8</td>
<td>1400</td>
</tr>
<tr>
<td>Phosphate</td>
<td>( 5.4 \times 10^{12} )</td>
<td>4.7</td>
<td>1200</td>
</tr>
<tr>
<td>Silicate</td>
<td>( 1.4 \times 10^{12} )</td>
<td>4.7</td>
<td>1100</td>
</tr>
<tr>
<td>Germanate</td>
<td>( 3.4 \times 10^{10} )</td>
<td>4.9</td>
<td>900</td>
</tr>
<tr>
<td>Tellurite</td>
<td>( 6.3 \times 10^{10} )</td>
<td>4.7</td>
<td>700</td>
</tr>
<tr>
<td>Fluorozirconate</td>
<td>( 1.59 \times 10^{10} )</td>
<td>5.77</td>
<td>500</td>
</tr>
<tr>
<td>LaF(_3) (cryst)</td>
<td>( 6.6 \times 10^8 )</td>
<td>5.6</td>
<td>350</td>
</tr>
<tr>
<td>Sulfide</td>
<td>( 10^6 )</td>
<td>2.9</td>
<td>350</td>
</tr>
</tbody>
</table>
Multiphonon Emission Rate Via Energy Gap

![Graph showing multiphonon emission rate vs. energy gap for different materials such as Borate, Phosphate, Silicate, Germanate, Tellurite, ZrF₄ glass, LaF₃ crystal, and Sulfdie. The y-axis represents the multiphonon emission rate in s⁻¹, and the x-axis represents the energy gap in cm⁻¹.](image-url)
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 maximum phonon-energy stays the same.

3. Quantum Yield

Radiative quantum yield from the metastable $^3F_4$ 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 properties in practical fibre device applications.