$LiGdF_4$ Transparent Oxyfluoride Glass-ceramics for Optical Applications

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Introduction

Transparent oxyfluoride glass-ceramics (TGCs) doped with rare earth ions (RE^{3+}) are one of the most promising classes of materials for high efficiency photoluminescence (PL) conversion from infrared (IR) and other light sources. TGCs are well suited for using in telecommunications and optoelectronics because of their transparency, mechanical and chemical resistance, low phonon energies and low refractive index inherited from fluoride crystals [1]. To achieve the transparency of GCs, crystal size, morphology, isotropic crystalline phases and their homogeneous distribution in glass matrix need to be strictly controlled [2]. Li^+ ions are regarded as an alternative to Na^+/K^+ in the crystalline phases of scheelite-type tetragonal (bipyramidal) morphology [3,4]. In particular, $LiGdF_4$ crystals are considered a suitable matrix for trivalent RE^{3+} ions with high capacity for isomorphic replacement of Gd^{3+} ions by other RE^{3+} ions due to their similar ionic radii without strong effect on the lattice structure. With the smaller cationic radius compared to Na^+/K^+, and higher cation polarization power, the substitution of Li^+ can increase the crystal field asymmetry around the trivalent lanthanide ions, thus significantly affecting the emission intensity as reported recently [5].

Experiments

Composition (%mol.)
- 40 SiO_2-25 Al_2O_3-18 Li_2O-7 LiF-10 GdF_3

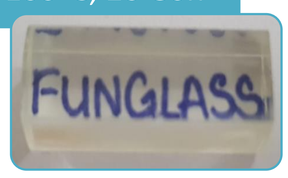
→ **Mechanical mixing, 1h**

→ **Calcination, 1200°C, 1h**

→ **Melting 1550°C, 2h**
- Several mixing: homogenized melt

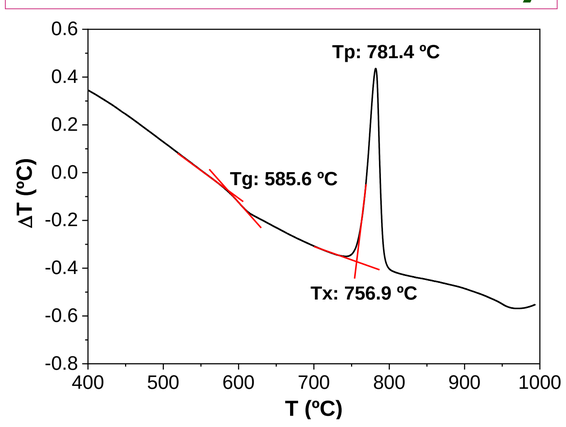
→ **Casting on brass mold**

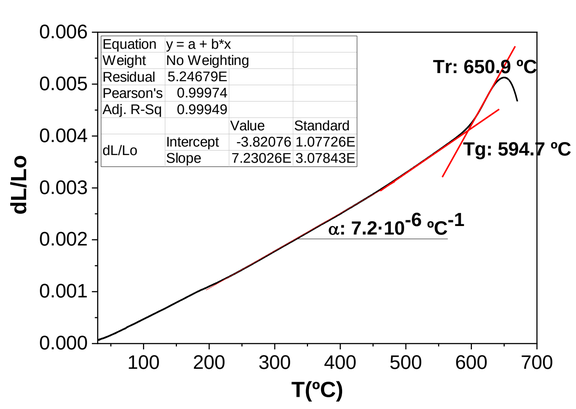
→ **Heat treating at T_g+100°C, 20-80h**



Results

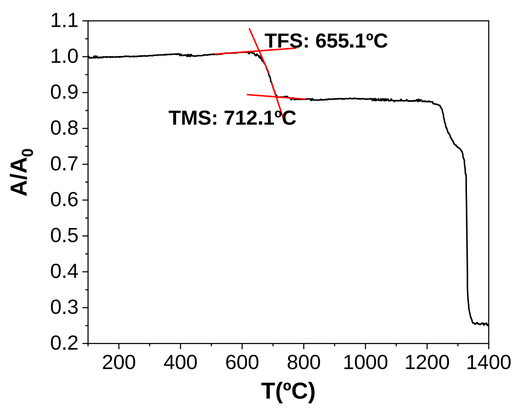
DTA and Dilatometry





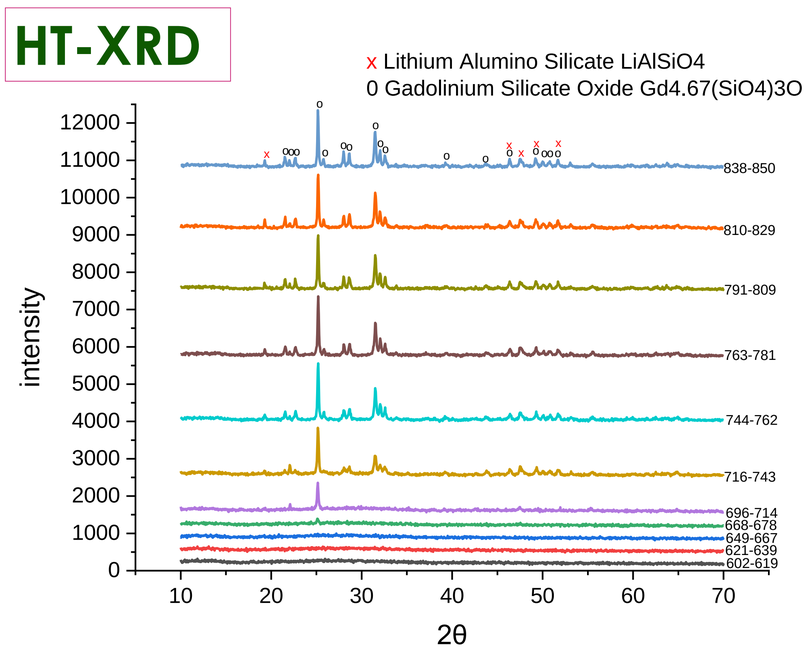
Glass T_g is 595°C, thermal treatments at temperatures between T_g and T_g+100°C will be used to obtain the corresponding glass-ceramics.

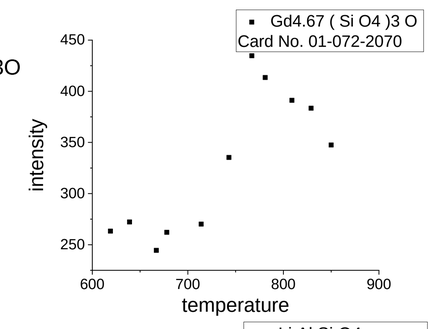
HSM

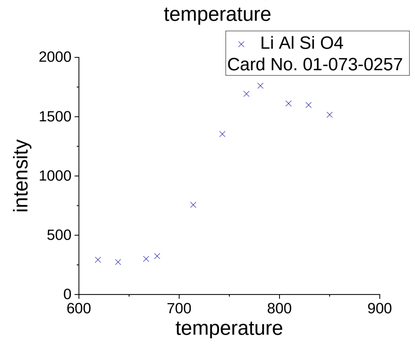


HSM provide the sintering range of the glass powder for processing through spark plasma sintering

HT-XRD



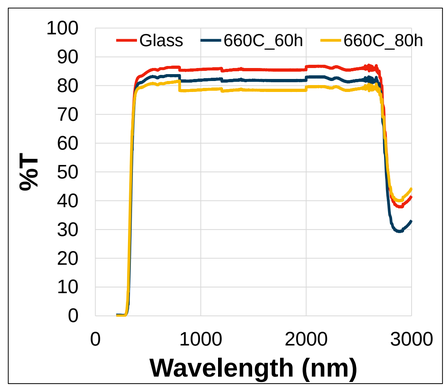




No fluoride phases are detected. The growth of Gadolinium Silicate Oxide and Lithium Alumino Silicate begin slightly over 600°C and peak at around 760 and 785°C, respectively. After 850°C, there was no discernible difference.

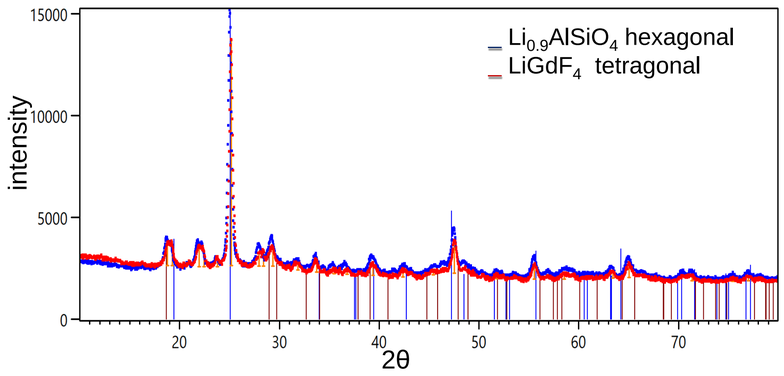
Transparency (%T)

Compared to the glass sample, %T ~85%, the heat treated GCs at 660°C for 60 h and 80 h get lower transparency with %T are around 80%, remain their transparency in NIR and visible regions.



XRD

Heat treated GCs at 660°C for 60 h (red) and 80 h (blue) confirm the formation of $LiGdF_4$ tetragonal around 8 and 10% respectively.



Conclusion

- ✓ Due to the very tiny crystal sizes, which are significantly smaller than the wavelength of visible light, the GCs products are transparent in mid-infrared and visible zones, with a percent T of roughly 80% when compared to their parent glass.
- ✓ Containing meta-stable $LiGdF_4$ tetragonal crystals with %wt. around 8% at low temperature treatment, but cannot observe the fluorine phase for quick scan (5°C/min) at high temperature and short time treatment in HT-XRD results.
- ✓ The final GC products present as good hosts for further doping to achieve luminescence properties.

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References

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