Making Transparent Er3+-Yb3+ Ions Doped Oxyfluoride Glass-Ceramics with Enhanced Luminescence via heat-treatment

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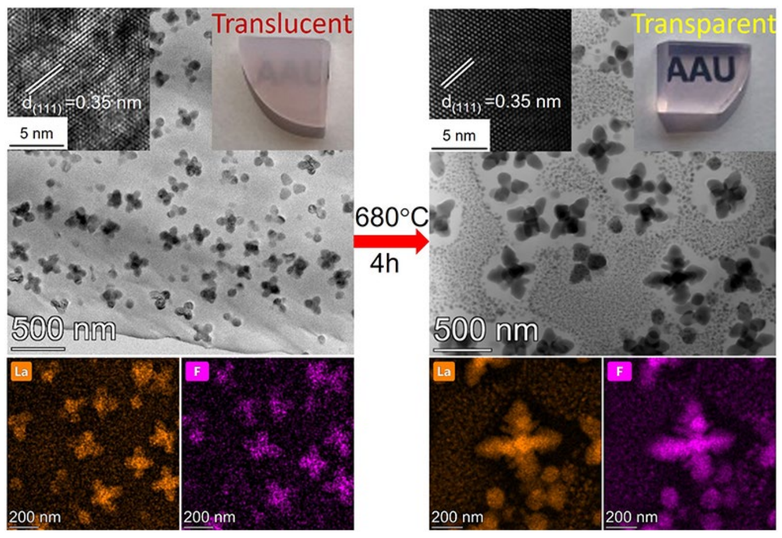
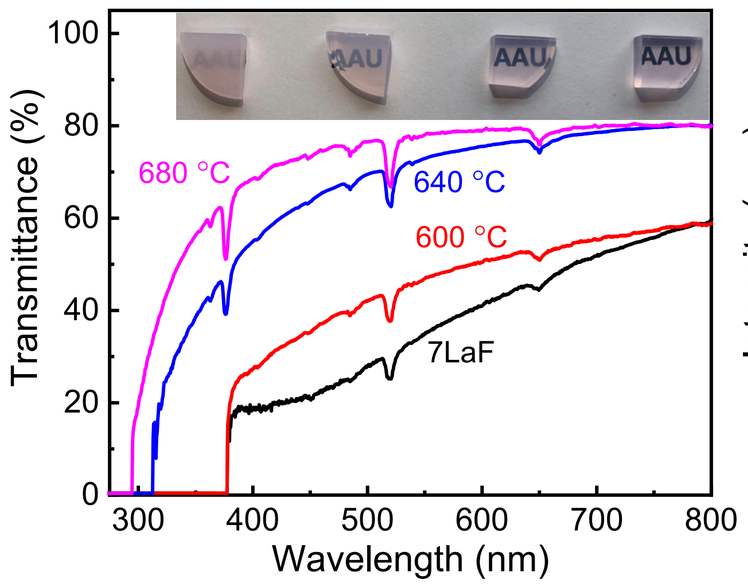
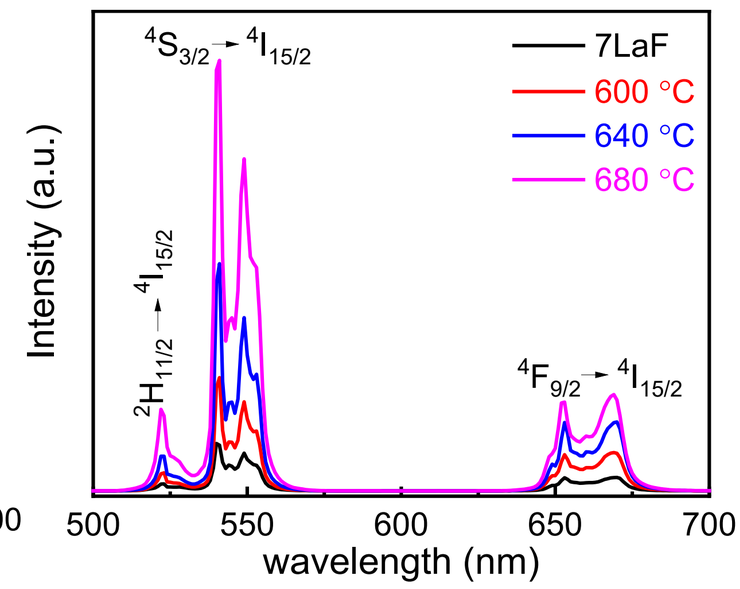


Abstract

It is known that the optical transparency of an oxide glass decreases with an increase of the size and fraction of crystals in the glass during heat-treatment (HT). Here we report an opposite scenario, where a translucent Er^{3+}-Yb^{3+} doped oxyfluoride glass-ceramic (GC) becomes transparent with increasing crystal size and crystallinity. Specifically, in the heat-treated GC samples, we observed that the growth of the existing Ba_2LaF_7 crystals and particularly the formation of small spherical Ba_2LaF_7 crystals greatly enhanced the light transmittance. The results show that the composition of the residual glass phase was altered (e.g., depletion of F^- and La^{3+}) in the way that the differences in refractive index between the glass matrix and the crystals are greatly reduced. As a consequence, the light scattering of the heat-treated GC was suppressed, and hence, the derived GC became transparent. In addition, a proper HT can also enhance the luminescence of the studied GC system.

Light Transmittance and Up-conversion (UC) Luminescence





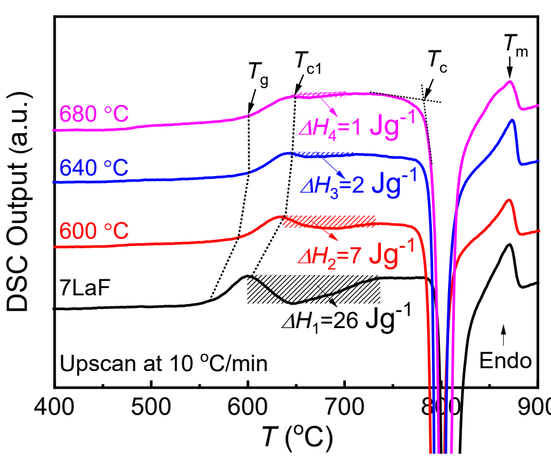
Light transmittance and UC Luminescence:

- Light transmittance increases upon HT.
- UC luminescence is 9 times higher than the 7LaF sample.

- **Two conditions for producing high transparent oxyfluoride GCs**

1. Nanocrystals should be considerably smaller (< 50 nm) than the wavelength of visible light
2. The difference in refractive index between nanocrystals and residual glass phase should be minimized (< 0.01) ★

DSC, XRD and Raman spectroscopy Characterizations



DSC:

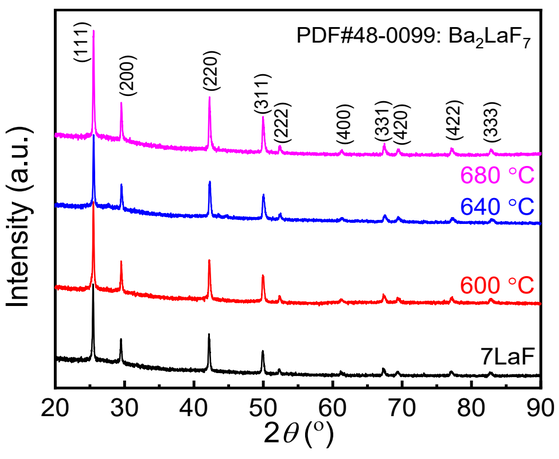
- T_g and T_{c1} increase with increasing HT temperature, whereas ΔH decrease, meaning that glass network connectivity and crystallinity increase upon HT

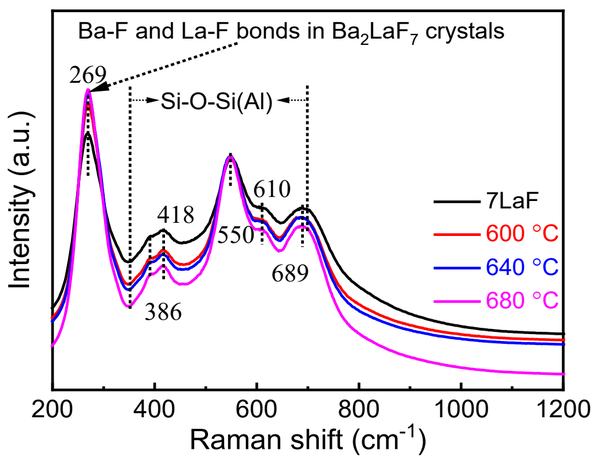
XRD:

- Only Ba_2LaF_7 crystals form upon HT.

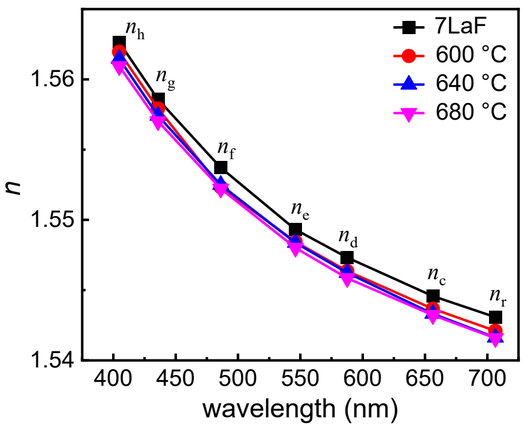
Raman spectra:

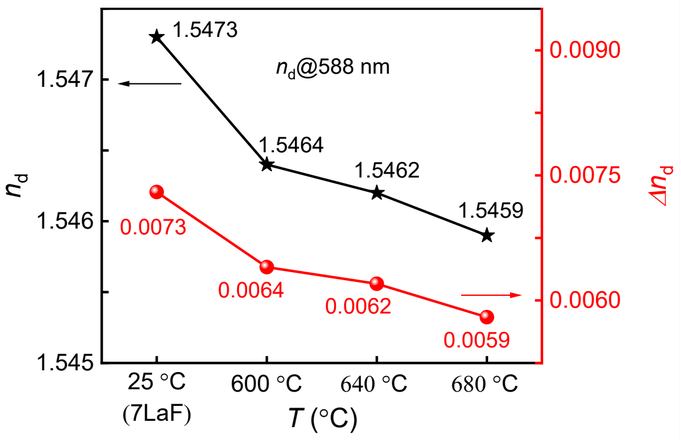
- The ratios between the intensities of 269 cm^{-1} and 549 cm^{-1} increase upon HT.

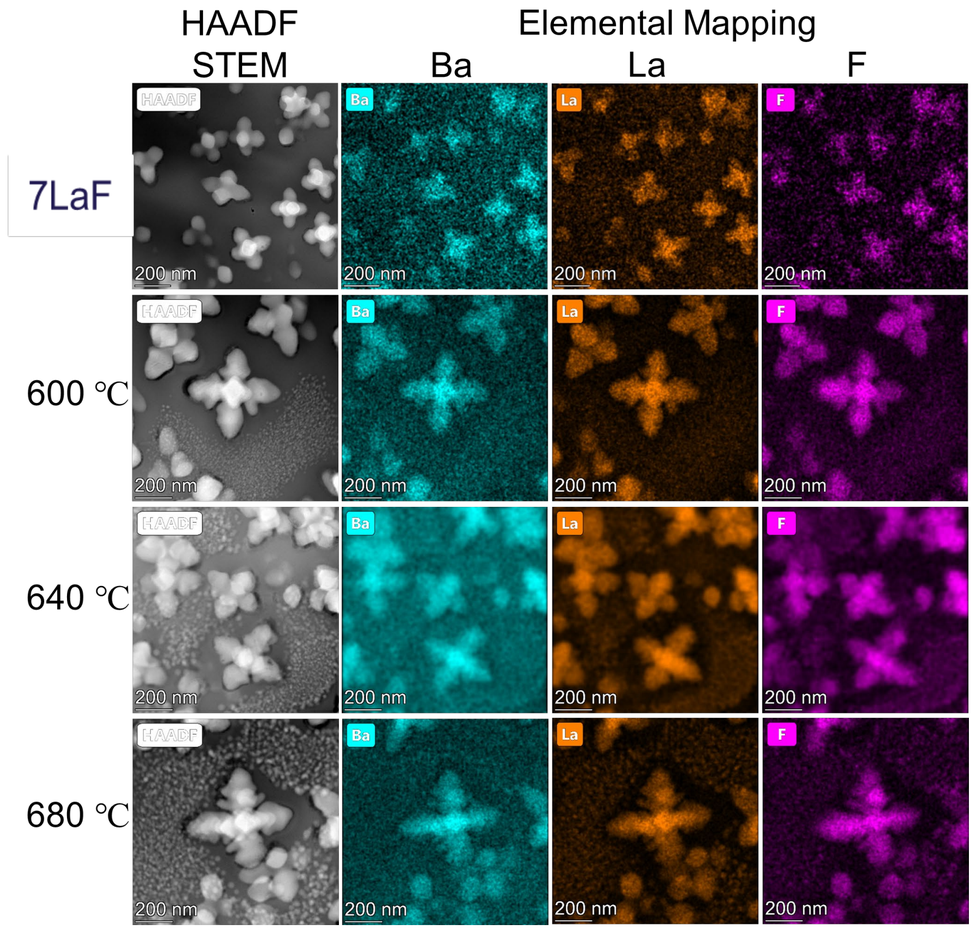




Refractive Index and EDS Mapping Characterizations







Refractive index (n):

- n decreases upon HT
- n_d of Ba_2LaF_7 crystal is 1.54
- n_d difference (Δn_d) is 0.0059, which is < 0.01

STEM and EDS Mapping

- Flower-like and tiny Ba_2LaF_7 crystals grow with HT.
- Most La^{3+}, F^- ions, and few Ba^{2+} ions diffuse from glass phase to Ba_2LaF_7 upon HT.

Conclusions

- A translucent Er^{3+}-Yb^{3+} doped oxyfluoride GC containing large flower-like Ba_2LaF_7 crystals is prepared via melt-quenching.
- The translucent oxyfluoride GC becomes transparent with increasing the crystal size and crystallinity as a result of HT, which is attributed to the suppression of the light scattering.
- The derived transparent GCs show strong UC luminescence.

Acknowledgements

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