Poster

Synthesis and structure of highly non-stoichiometric garnets $RE_{3+x}Al_{5-x}O_{12}$ (0 < x < 0.6)

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Rare-earth aluminates $RE_3Al_5O_{12}$ with the cubic garnet structure are an important class of optical materials with a range of technological applications. When formed under typical reaction conditions as ceramics or single crystals, these materials do not tolerate large deviations from ideal $RE_3Al_5O_{12}$ stoichiometry, and exhibit well-characterised luminescence responses based on the identity of the rare-earth and/or transition metal dopants. We have recently shown that containerless melt-quenching – a non-equilibrium synthesis method – can be used to induce major deviations from ideal stoichiometry in these systems, yielding compositions of type $RE_{3+x}Al_{5-x}O_{12}$ with $0 \leq x \leq 0.60$ for $RE = Y^{3+}$ or Gd^{3+} [1,2]. These materials crystallise from glasses or super-cooled melts at ~900°C, and decompose on heating above ~1300°C (far below typical ceramic synthesis temperatures of ~1650°C). The garnet structure is retained across the full compositional (x) range, with the excess RE^{3+} accommodated on the octahedral (6-coordinated) sites of the Al^{3+} sublattice. This crystal chemistry has implications for the luminescence properties, because it allows rare-earth activators to be distributed over two cation sublattices. This has a strong impact in up-conversion systems featuring small rare-earth activators (such as Er^{3+}) with an affinity for octahedral coordination, whose colours shift as a function of non-stoichiometry (x). On the other hand, its impact in down-conversion systems with large rare-earth activators (such as Ce^{3+}) is somewhat limited, as such cations tend to occupy only the 8-coordinate *A* sublattice. *Note that the distribution of the activator species over A and B sublattices is particularly challenging to determine crystallographically, due to weak X-ray scattering contrast with the host RE^{3+} ions,* and this is addressed with a complementary multi-technique approach using XRD, X-ray absorption spectroscopy and simulations. The existence of $Y_{3+x}Al_{5-x}O_{12}$ and $Gd_{3+x}Al_{5-x}O_{12}$ implies that highly non-stoichiometric garnets should be realisable across the 4*f* series under suitable reaction conditions, highlighting the potential for colour tuning of new up-conversion phosphors by control of host stoichiometry.

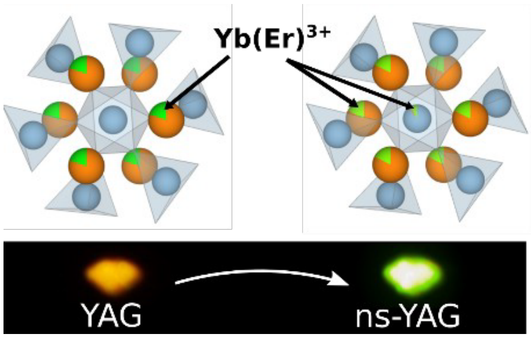

Figure 1. Distribution of Er^{3+} over two cation sublattices in highly non-stoichiometric YAG:Er upconversion phosphors strongly influences the emission colour (in this case shifting from red to green emission).

[1] W. Cao, A. I. Becerro, V. Castaing, X. Fang, P. Florian, F. Fayon, D. Zanghi, E. Veron, A. Zandona, C. Genevois, M. J. Pitcher and M. Allix *Advanced Functional Materials* **33**, 2213418 (2023).

[2] X. Fang, V. Castaing, A. Becerro, W. Cao, E. Veron, D. Zanghi, M. Dyer, C. Genevois, M. Allix and M. Pitcher *ChemRxiv* 10.26434/chemrxiv- 2024-1s1wc (2024).