Garnet compounds are very attractive host materials for optical applications such as scintillators, phosphors and lasers. The \{A^3+\}\{B^3+\}\{C^3+\}O_{12} garnets are oxide structures with cubic symmetry and the locations of the cations over the AO8 dodecahedral {24c}-, BO6 octahedral (16a)- and CO4 tetrahedral (24d)- sites are potential research objects for the study of luminescence centers designed by substitution and defects. In particular, our group has recently reported that the highly nonstoichiometric Y_{3+x}Al_{5-x}O_{12} (0 \leq x \leq 0.4) garnet can exhibit up to 20% of AlO6 occupied by excess Y3+, breaking the conventional \leq 1% deviation from the stoichiometric Y3Al5O12 limit and contributing to the dopant distribution on the AO8 and BO6 sublattices, which has been determined to be responsible for the modulation of the luminescent colour.\( ^{(1)}\) As a member of the garnet family, Gd3Al5O12 (GAG) has been extensively investigated for potential applications in optical materials due to lower electronegativity and higher theoretical density of Gd3+, which is optically better than the well-known YAG. In addition, Gd3+ (0.938 Å) with larger ionic radii compared to Y3+ (0.90 Å) potentially offers possibilities for larger dopants to occupy the AlO6 site in nonstoichiometric GAG. Therefore, the structural study of highly nonstoichiometric GAG may provide a new idea for subsequent exploration of a range of non-stoichiometric garnet material for optical applications.

Here, the crystallization from glass synthesis method, using aerodynamic levitation (ADL) coupled with laser heating to prepared glass was used to synthesize a new series of highly non-stoichiometric Gd3+xAl5-xO12 solid solutions with an unprecedented composition range of 0 \leq x \leq 0.6. Synchrotron powder diffraction (SPD) average structure and extended X-ray absorption fine structure (EXAFS), transmission electron microscope (TEM) local structure studies confirmed that about 30% six coordinated Al3+ in ns-GAG is replaced by excess Gd3+, which allows the dopant ion RE3+ (RE3+ = Tb3+, Er3+, Tm3+, Yb3+) to partially disorderly occupy the AlO6 site, forming six coordinated REO6 luminescent centers. Furthermore, systematic spectroscopic studies have shown the differentiated sensitivity of dopant RE3+ (RE3+ = Ce3+, Tb3+, Er3+, Tm3+, Ho3+) to (1) inequivalent AO8 sites around different BO6 neighbours configurations and (2) BO6 sites in non-stoichiometric GAG in terms of variations of emission spectra and luminescence colour. Hence, the highly non-stoichiometric GAG study provides a research basis for performance enhancement and luminescent colour modulation of commercially viable garnet-based optical materials. In addition, the further exploration and research of highly non-stoichiometric GGG frustrated magnetic materials and non-stoichiometric GAGG persistent materials are in process.


*Speaker
**Keywords:** highly nonstoichiometric garnet, GAG, ADL, crystallization from glass, multiple RE3+ sites, phosphor