
Structure and multiple RE3+ luminescence sites of highly nonstoichiometric GAG

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Abstract

Garnet compounds are very attractive host materials for optical applications such as scintillators, phosphors and lasers. The $\{A3+\}3(B3+)2(C3+)3O12$ 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 $Y3+xAl5-xO12$ ($0 \leq x \leq 0.4$) 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.

(1) Weiwei Cao, Ana Isabel Becerro, Victor Castaing, Xue Fang. *et al.* Advanced function materials, 2023. <https://doi.org/10.1002/adfm.202213418>.

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