Stabilization of Cr^{4+} near-infrared luminescence through eutectic crystal engineering

Eutectic microstructures provided an effective strategy for tuning luminescence through phase coupling. The $Y_3Al_5O_{12}$–$YAlO_3$:Cr,Mg eutectic crystal grown by the micro-pulling-down method exhibited a well-defined lamellar microstructure, markedly broadened Cr^{4+} R-line emission and exclusively Cr^{4+} luminescence. By contrast, the uPD-grown $Y_3Al_5O_{12}$:Cr,Mg single crystal was phase-pure garnet and showed well-resolved Cr^{4+} R-lines together with concurrent Cr^{3+} and Cr^{4+} emissions. These findings established phase-coupled eutectics as an effective approach for tailoring Cr-based functional materials.

Broadband Cr^{4+} luminescence is attractive for near-infrared (NIR) photonics, yet its stabilization, efficiency and local-site control remain poorly understood [1]. We investigated whether eutectic phase coupling in the Cr,Mg-doped $Y_3Al_5O_{12}$–$YAlO_3$ (YAG–YAP:Cr,Mg) system could promote Cr^{4+} stabilization and enable optical functionality inaccessible in conventional $Y_3Al_5O_{12}$:Cr,Mg (YAG:Cr,Mg) single crystals [2]. Fig.1A shows photographs of the as-grown YAG:Cr,Mg single and YAG–YAP:Cr,Mg eutectic crystals. The dark brown color of both samples indicated a dominant fraction of Cr^{4+} ions [3]. SEM–EDS mapping (Fig. 1B) reveals high elemental homogeneity in the single-crystal and well-defined lamellar eutectic microstructure in the composite. Powder XRD (Fig. 1C and 1D) confirms phase-pure garnet YAG in the single crystal and the coexistence of YAG and YAP in the eutectic

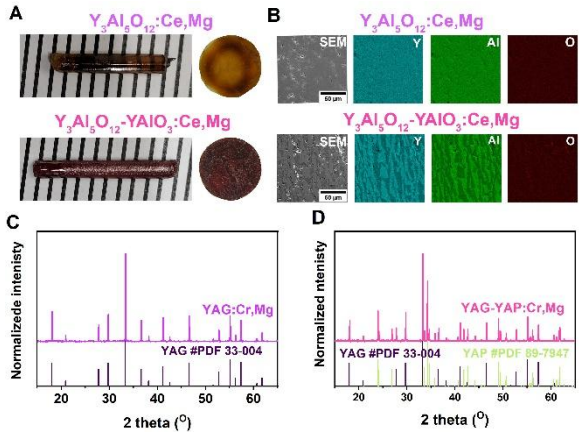

Fig. 1 (A) Photographs of the as-grown YAG:Cr,Mg single crystal (top) and YAG–YAP:Cr,Mg eutectic crystal (bottom), together with polished plates. (B) SEM micrographs and EDS elemental maps (Y, Al and O). Powder XRD patterns of (C) YAG:Cr,Mg and (D) YAG–YAP:Cr,Mg crystals.

Figure 2a shows the characteristic Cr^{4+} absorption bands in YAG:Cr, whose strong absorption in the visible range accounted for the brown coloration [3]. Under 980 nm excitation, both YAG:Cr and YAG–YAP:Cr exhibited broad near-infrared Cr^{4+} emission, whereas the eutectic

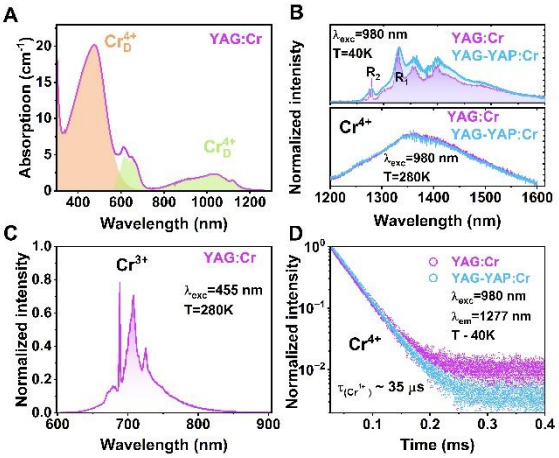

Fig. 2 (A) RT absorption spectrum of YAG:Cr showing Cr^{4+} bands. (B) Cr^{4+} emission spectra of YAG:Cr and YAG–YAP:Cr under 980 nm excitation at 40 and 280 K. (C) Cr^{4+} emission spectrum of YAG:Cr at 280 K under 455 nm excitation. (D) Cr^{4+} emission decay of YAG:Cr and YAG–YAP:Cr at 40 K (λ_{exc}=980 nm, λ_{em}=1277 nm).

shows broader low-temperature R-line emission (Fig. 2B), consistent with a broader distribution of local crystal fields. By contrast, Cr^{3+} emission was observed exclusively in YAG:Cr under 455 nm excitation (Fig. 2C). Time resolved measurements revealed similar Cr^{4+} decay kinetics in both samples, with a lifetime of ~35 µs at 40 K (Fig. 2D). These results show that eutectic phase coupling broadened the Cr^{4+} R-line emission and enabled complete conversion of Cr^{3+} to Cr^{4+}. Eutectic engineering therefore emerged as a promising strategy for achieving exclusively Cr^{4+} luminescence for advanced photonic applications.

Acknowledgment

This work was supported by ICC-IMR, Tohoku University.

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Keywords: crystal growth, luminescence, infrared (ir) spectroscopy
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