

COMMENT

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Chen *et al.* (*J. Mater. Chem. C*, 2018, **6**, 10687–10692) reported that the emission of Tb³⁺ in Sr₈ZnSc(PO₄)₇:Tb³⁺ shows zero-thermal-quenching behavior at high temperature (up to 200 °C), which was attributed to the compensation of the emission intensity loss by carriers from different trap depths. In this comment, we argue that this unique behavior is just an intrinsic property of Tb³⁺, and the strategy of sensitization by other ions like Ce³⁺ is needed to make Tb³⁺ activated luminescence materials usable for phosphor converted white LEDs.

Significant zero-thermal-quenching was first reported in Na₃Sc₂(PO₄)₃:Eu²⁺, and it was attributed to a trap related mechanism, which refers to energy transfer from thermally activated traps to luminescent centers as the temperature is increased.^{1,2} Since then, the trap related mechanism has attracted increasing attention because it can assist phosphors in keeping a high quantum efficiency at high temperature and exhibiting great potential for high power LED applications. Accordingly, the zero-thermal-quenching model is important only for efficient phosphors. Recently, Chen *et al.*³ reported zero-thermal-quenching behavior of a Tb³⁺ doped Sr₈ZnSc(PO₄)₇ phosphor. Some supporting evidence is questionable, so further comments are needed.

After reading through the commented paper in ref. 3, the requisite quantum efficiency of Sr₈ZnSc(PO₄)₇:Tb³⁺ was not provided. Instead, an extremely low quantum efficiency of Sr₈ZnSc(PO₄)₇:Tb³⁺ phosphor can be inferred from the lifetimes of the ⁵D₃ and ⁵D₄ levels, which were measured to be only 0.90 and 1.17 ns in the Sr₈ZnSc(PO₄)₇:0.02Tb³⁺ phosphor. In general, the radiative lifetimes of ⁵D₃ and ⁵D₄ are in the order of two microseconds (ms),^{4–6} and even in the lanthanide complexes,⁷ the radiative lifetime of ⁵D₄ is more than 0.1 ms. If the measured fluorescence decay curves are the real response of fluorescence signals, the ultrashort lifetimes mean that there is a very fast nonradiative process to depopulate the emitting states, thus resulting in a very low quantum efficiency.

The PL spectra of Sr₈ZnSc(PO₄)₇:Tb³⁺ for various Tb³⁺ concentrations at room temperature and the increase in ⁵D₃–⁷F_J (*J* = 0–6) emission intensities with the increase of Tb³⁺ concentration up to 10% are shown in Fig. 2 of ref. 3. The result is attributed to the effect of energy transfer from a trap to Tb³⁺. However, the trap cannot be thermally activated at room temperature based on the thermo-luminescence spectra shown in Fig. 4(d) of ref. 3, and it should be noted that the backgrounds in their PL spectra are enhanced with increasing temperature, leading to an untrue increment for ⁵D₃–⁷F_J (*J* = 0–6) emission intensity. The emission spectra of Sr₈ZnSc(PO₄)₇:Tb³⁺ at various temperatures ranging from 25 °C to 250 °C were also measured and their emission intensities of ⁵D₃–⁷F_J (*J* = 0–6) transitions show an upward trend with increased temperature as shown in Fig. 4 of ref. 3. However, the connection of energy transfer from the trap to Tb³⁺ failed to be established. The observation of the initial increase and subsequent decrease in the ⁵D₃ lifetimes with the increase of Tb³⁺ concentration shown in Fig. 3 of ref. 3 lacks theoretical basis because the energy level lifetime of Tb³⁺ as an acceptor, in principle, is independent of energy transfer. Moreover, the measured decay curves and the obtained lifetimes need to be further confirmed.

The origin of the high thermal stability of the Tb³⁺ emission has been studied in detail in several previous studies.^{8–12} The fluorescence lifetimes of Tb³⁺ are not shortened at all from room temperature to 483 K upon Ce³⁺ excitation (shown in Fig. S1, ESI†), indicating a highly thermally stable emission of Tb³⁺, because of the large energy gap (about 15 000 cm^{–1}) between the emitting level ⁵D₄ and its next lower level ⁷F₁.¹² The single Tb³⁺ doped Ba₂Y₅B₅O₁₇ (BYBO) and Ba₂Lu₅B₅O₁₇ (BLBO) were synthesized for comparison. The temperature dependent PL spectra of BLnBO (Ln = Y, Lu):Tb³⁺ with negligible backgrounds

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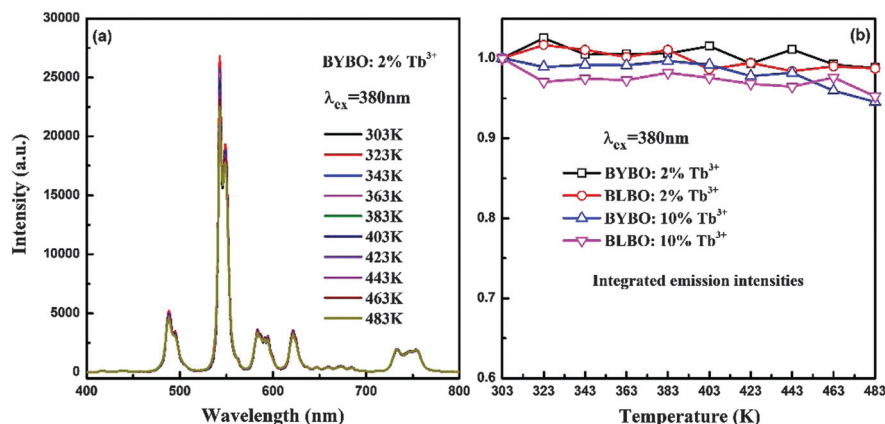


Fig. 1 (a) Temperature dependent PL spectra of BYBO:2%Tb³⁺. (b) The temperature dependencies of the integrated emission intensities of BLnBO:xTb³⁺ (Ln = Y, Lu; x = 2%, 10%) upon 380 nm excitation.

were measured, as shown in Fig. 1(a) and Fig. S1–S3 (ESI[†]). Obviously, BLnBO (Ln = Y, Lu):Tb³⁺ also shows almost zero-thermal-quenching as shown in Fig. 1(b), although there is no charge mismatch between Y³⁺/Lu³⁺ and Tb³⁺ to bring about the traps. Therefore, the excellent thermally stable emission of Tb³⁺ just results from the intrinsic properties of f–f transitions rather than the assistance of the traps. Finally, considering their low absorption of short-wavelength visible light, the strategy of sensitization by other ions like Ce³⁺ is needed to make Tb³⁺ activated luminescence materials usable for phosphor converted white LEDs.¹²

Conflicts of interest

There are no conflicts of interest to declare.

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