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Reply to Comment on “Breakdown of Crystallographic Site Symmetry in Lanthanide-Doped NaYF$_4$ Crystals”**

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Karbowiak et al. recently commented on our Communication “Breakdown of Crystallographic Site Symmetry in Lanthanide-Doped NaYF$_4$ Crystals”.[1] They attempted to criticize the crystal-field (CF) analysis of Eu^{3+} in disordered NaYF$_4$ based on their surmise. Unfortunately, there are numerous misunderstandings in their correspondence.[2] In this reply, we respond to their comment and clarify our interpretations of the issues they raised.

Regarding the adoption of the CF parameters (CFPs) of Eu^{3+} in Gd$_2$O$_3$ as the starting values in the fit, it is true that the coordination environments of Gd$_2$O$_3$ and NaYF$_4$ host are somewhat different. However, it should be pointed out that both α- and β-NaYF$_4$ are disordered crystals, where the site symmetry of Y^{3+} is O_h and C_{3h}, respectively.[3] Once Eu^{3+} ions are doped into such disordered crystals to substitute for Y^{3+}, the symmetry of spectroscopic sites of Eu^{3+} may differ drastically from that of crystallographic sites of Y^{3+}, which is due to the mismatch of ionic radius between Eu^{3+} and Y^{3+}.[4] The local site symmetry of Eu^{3+} in NaYF$_4$ can be revealed by the high-resolution emission spectra (Figure 1), selective excitation spectra, and photoluminescence (PL) decays at low temperature (Supporting Information, Figure S1). Note that our emission pattern of β-NaYF$_4$:Eu^{3+} is consistent with that reported by other groups.[5] For instance, the line positions and splittings reported by Jia et al. are nearly identical to our results (Figure 1). In the PL pattern, the most crucial fingerprint to corroborate the low site symmetry in NaYF$_4$:Eu^{3+} crystals is the appearance of the $^5D_0 \rightarrow {}^7F_0$ peak. Furthermore, three and five CF transition lines of $^5D_0$ to $^7F_1$ and $^7F_2$ were observed, which demonstrated the highest site symmetry of Eu^{3+} in β-NaYF$_4$, distorted from C_{3h}, should be C_s. Such breakdown of crystallographic site symmetry in Eu^{3+}-doped NaYF$_4$ crystals was not only corroborated by these PL spectra, but also confirmed by the CF level fitting.

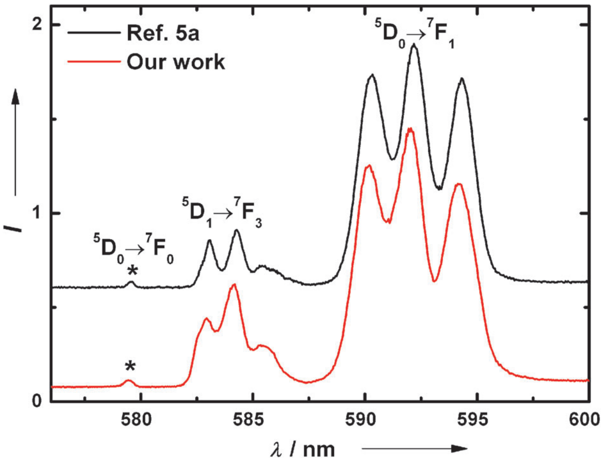

Figure 1. 10 K PL emission spectra of β-NaYF$_4$:Eu^{3+} reported in Ref. [5a] (upper) and our original work (lower), respectively. The CF transition line from $^5D_0$ to $^7F_0$ is marked by an asterisk.

To the best of our knowledge, until now no data on the CFPs of NaYF$_4$ or other disordered crystals with similar structure and local site symmetry are available. The choice of the set of CFPs values of Gd$_2$O$_3$ as the starting ones in the fit is technically feasible based on the following considerations. First, as mentioned in Ref. [1], the highest spectroscopic site symmetries of Eu^{3+} are found to descend from crystallographic O_h to C_s (or C_2) in α-NaYF$_4$, and from crystallographic C_{3h} to C_s in β-NaYF$_4$, respectively. Similar to the well-established CFP fitting strategy in this field,[6] to rationally reduce the number of freely varied CFPs in the fit, we performed the energy level fitting by reasonably assuming the highest site symmetry of C_s for both α- and β-NaYF$_4$ in view of the same set of allowed CFPs for the site symmetry of C_s or C_2.[7] Second, by using the CFPs of Gd$_2$O$_3$:Eu^{3+} as starting values,[8] the energy-level fitting yielded a relatively small root-mean-square deviations for α- and β-NaYF$_4$, namely, 13.5 and 13.8 cm^{-1} (with energy shifts in a range of 0–30 cm^{-1} for most of the levels), respectively, an important indicator for the goodness of the fit.[9] Note that total 48 CF levels of Eu^{3+} in α-NaYF$_4$, instead of 41 levels as they criticized in their comment, were included in our fit.

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As for the fitting results, it is not unusual for certain discrepancy between the starting CFP values and the fitted ones, because many freely varied CFPs and free-ion (FI) parameters (19 parameters in our case) were optimized by least-squares fit to the observed levels.[9] Even by adopting the CFPs from crystals with similar structure as starting ones, sometimes it is difficult to attain a good agreement between the starting and fitted CFPs.[6,10] To exemplify this, in their recent work by Karbowiak et al.,[10b] the fitted CFPs of $LaAlO_3$:Nd^{3+} differed significantly from the starting ones of $YAlO_3$:Er^{3+}: among six CFPs for the site symmetry of D_3, two CFPs (B_{20} and B_{40}) had different signs, and the remaining four CFPs (B_{43}, B_{60}, B_{63}, and B_{66}) changed their values remarkably.

Karbowiak et al. attempted to use the second moments σ_2(SLJ) as the criterion for the CF parameterization. Nevertheless, the difference between the observed and calculated σ_2(SLJ) of $^7F_1$ reflected only the deviation for one specific multiplet instead of the whole multiplets of interest. As such, σ_2(SLJ) is rarely adopted as a criterion to assess the validity of the fitting results.[7] Even in their own work, Karbowiak et al. did not use this criterion to check the consistency between the observed and fitted values.[10b]

In summary, more evidence such as high-resolution PL spectra and PL decays has unambiguously verified the breakdown of crystallographic site symmetry in Eu^{3+}-doped $NaYF_4$ crystals. The rationality of our CF level fitting has been clarified. Although Karbowiak et al. raised technical issues concerning the CF level fitting in disordered crystals that deserve further studies, these are, to a large extent, motivated by a misinterpretation of our conclusions. The critique as a whole does not compromise the conclusions originally drawn in our paper.

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