Comment on “Spectra and energy levels of Er$^3+$ (4f$^{11}$) in NaBi(WO$_4$)$_2$”
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A recent article by Gruber et al. [Gruber, J. Appl. Phys. 94, 7128 (2003)] reports the measurements of the optical absorption and photoluminescence spectra of Er$^3+$ in NaBi(WO$_4$)$_2$ (NBW), and the results of the interpretation and fitting of the observed crystal-field (CF) splitting of Er$^3+$ multiplets with a quasicenter model. In the light of available, previously published information, we argued that these conclusions are not warranted. As a proof, the composition of the Er$^{3+}$-NBW wave functions and the energy levels derived from the final obtained CF parameters have been checked through the simulation of the temperature-dependent paramagnetic susceptibility $\chi_m$ according to the Van Vleck formalism and, unfortunately, experimental curves of $\chi_m$ versus $T$, measured in parallel and perpendicular directions to the $e$ axis of the NBW crystal, were not adequately reproduced. The same simulation was carried out with a set of free ions and CF parameters resulting from our previous polarized CF analysis of Er$^{3+}$ in a NBW crystal, and the agreement with the measured $\chi_m$ versus $T$ curves is a clear indication of the validity and physical meaning of our earlier performed CF analysis. © 2004 American Institute of Physics. [DOI: 10.1063/1.1792382]

A recent article by Gruber et al.$^1$ reports the measurements of the optical absorption (OA) and photoluminescence (PL) spectra of Er$^3+$ in NaBi(WO$_4$)$_2$ (NBW), and the results of the interpretation and fitting of the observed crystal-field (CF) splitting of Er$^3+$ multiplets with a quasicenter model.

Contrary to the belief of these authors, after the paper of Kaminskii et al.$^2$ a continuous effort has been undertaken to study the properties of NBW single crystals. This effort included aspects related to the synthesis and crystal-growth procedures;$^3$–$^6$ the structural characterization,$^7$ which corrects previous$^8$ space-group assignments; the anisotropic linear optical properties such as refractive indices,$^4$ infrared absorption and Raman spectra,$^9$ and scintillating capability,$^{10}$–$^{14}$ the nonlinear optical properties such as Raman shifting$^{15}$ and up conversion,$^{16}$ and finally, the detailed spectroscopy and CF analyses of several rare-earth R$^3+$ impurities, namely, Er$^3+$,$^{17}$Nd$^3+$, Pr$^3+$, Nd$^3+$, and Yb$^{3+}$, in NBW crystals.

From the published information, the following are now well established:

(a) The tetragonal structure of NBW belongs to the noncentrosymmetric space group $I4$ (No. 82), $Z=2$, with the Na$^+$ and Bi$^{3+}$ cations sharing two nonequivalent crystal sites, $2b$ and $2d$, both with an $S_4$ point symmetry. One of these sites is preferentially occupied by Bi$^{3+}$, whereas the other contains a larger amount of Na$^+$ cations. Although in both sites Bi$^{3+}$ has an eightfold oxygen coordination, the Bi-O distances and O-Bi-O angles differ for these two sites. Since R$^3+$ ions replace Bi$^{3+}$, at least two different phenomena contribute to the large observed bandwidth of the R$^3+$ optical spectra: (i) the overlapping R$^3+$ contributions arising from these two sites and (ii) the broadening associated to the centers resulting from different short-range Na$^+$ and Bi$^{3+}$ distributions around each one of the two R$^3+$ sites mentioned previously.

(b) The presence of optical transitions associated to the polarization in the R$^3+$ optical spectra in NBW has been well documented for a number of ions. Figure 1 includes some selected examples for Er$^3+$, Nd$^3+$, and Pr$^3+$. The $S_4$ characteristics in the $\sigma$- and $\pi$-polarized spectra of Er$^3+$ in NBW are by no means weak but are strongly exhibited [see for instance the 10 K polarized OA spectrum corresponding to the $^{4}I_{15/2} \rightarrow ^{4}S_{3/2}$ transitions as it appears in Fig. 1(a)], and this situation is extensive to other Er$^3+$ transitions as shown in Fig. 3 of Ref. 17. This is a major point of the current comment because it is only from polarized low-temperature measurements of the optical spectra, through the attribution of the corresponding irreducible representations to the energy levels, which will be possible to correctly ascertain the splitting of $^{4}S_{3/2}$ for Er$^3+$ in NBW. The erroneous determination of the low-lying $^{4}S_{3/2}$ energy level in Ref. 1 leads to a poor description of the $^{4}I_{15/2}$ ground state of Er$^3+$ in NBW displayed in Fig. 4 and therefore to a systematic uncertainty on the hot bands described. A set of CF parameters derived from the phenomenological analysis of the optical spectra of Nd$^3+$ in NBW (and obviously its comparison with the results from more or less empirical models) does not constitute an adequate starting set for analyzing the CF splitting of Er$^3+$ in the same host. The explanation is related to the...
changes and distortions in the local symmetry created in the crystal when Bi\(^{3+}\) ions are substituted by larger Nd\(^{3+}\) (or Pr\(^{3+}\)) cations, which became evident in the polarized low-temperature OA and PL spectra for these cations in NBW. The optical spectra display features inconsistent with the S\(_4\) selection rules for the induced electric dipole and magnetic dipole transitions and are better described assuming an average C\(_2\) site symmetry and the corresponding 14 CF parameters defining this potential.\(^{19,20}\) However, when Er\(^{3+}\) cations are embedded in NBW, a well-defined S\(_4\) behavior is observed in both the \(\sigma\)- and \(\pi\)-polarized spectra.\(^{17}\) Additionally, the number of Nd\(^{3+}\) energy levels derived at 77 K in Ref. 2 is very limited, and discrepancies can be found with the more complete set of levels determined recently at 10 K.\(^{20}\)

On the other hand, it is well known that the determination of a consistent set of CF parameters and associated wave functions for the energy levels of a given 4f\(^N\) configuration allows the simulation of the thermal dependence of the paramagnetic molar susceptibility \(\chi_m\) for each direction of the R\(^{3+}\) point crystal site.\(^{22}\)

The experimental curves of \(\chi_m\) versus \(T\) measured in parallel \(\parallel\) and perpendicular \(\perp\) directions to the \(c\)-crystal axis, i.e., \(\parallel\) and \(\perp\) to the average fourfold-point symmetry axis of Er\(^{3+}\) in NBW (\([\text{Er}]=0.92\times10^{20} \text{ cm}^{-3}\)), are plotted in Fig. 2. Figure 2(a) shows the comparison with the corresponding \(\chi_m\) versus \(T\) curves calculated using the determined set of free ions and the S\(_4\) CF parameters for the Er-doped NBW crystal studied in Ref. 17. The same calculation has been also performed using the wave functions derived from the free ion\(^{23}\) and the final CF parameters achieved in Ref. 1, and these latter \(\chi_m^{-1}\) versus \(T\) curves are included in Fig. 2(b).

The good reproduction of the experimentally observed curves shown in Fig. 2(a) constitutes a successful test of the validity and physical meaning of our earlier CF analysis\(^{17}\) and a proof of the accuracy of the determined wave functions for Er\(^{3+}\) energy levels in the NBW host.
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