This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Roles of oxygen Frenkel pair in the photoluminescence of Bi\(^{3+}\)-doped Y\(_{2}\)O\(_{3}\): Computational predictions and experimental verifications

Heechae Choi\(^a\), So Hye Cho\(^b\), Sovann Khan\(^b\), Kwang-Ryeol Lee\(^a\) and Seungchul Kim\(^{a*}\)

Bi\(^{3+}\) as a dopant in wide-band-gap yttria (Y\(_{2}\)O\(_{3}\)) has been used as a green light emission center or a sensitizer of co-doped rare earth elements. Because the photoluminescence (PL) properties of Y\(_{2}\)O\(_{3}\):Bi\(^{3+}\) vary remarkably according to heat treatments, the roles of point defects have been an open question. Using first-principles calculations and thermodynamic modeling, we have thoroughly investigated the formation of point defects in Y\(_{2}\)O\(_{3}\):Bi\(^{3+}\) at varying oxygen partial pressures and temperatures, as well as their roles in the PL. The photoabsorption energies of the Bi\(^{3+}\) dopant were predicted to be 3.1 eV and 3.4 eV for doping at the S\(_6\) and the C\(_2\) sites, respectively, values that are in good agreement with the experimental values. It was predicted that an oxygen interstitial (O\(_i\)) and an oxygen vacancy (V\(_O\)) are the dominant defects of Y\(_{2}\)O\(_{3}\):Bi\(^{3+}\) at ambient pressure and an annealing temperature of 1300 K (3.19×10\(^{16}\) cm\(^{-3}\) for 1% Bi doping), and the concentrations of these defects in doped Y\(_{2}\)O\(_{3}\) are approximately two orders of magnitude higher than them in undoped Y\(_{2}\)O\(_{3}\). The defect V\(_O\)\(^{2+}\) in Y\(_{2}\)O\(_{3}\):Bi\(^{3+}\) was predicted to reduce the intensity of PL from Bi\(^{3+}\) at both S\(_6\) and C\(_2\) sites. We verify our computational predictions from our experiments that the stronger PL of both 410 and 500 nm wavelengths was measured for the samples annealed at higher oxygen partial pressure.

**Introduction**

Transparent bixbyite yttria (Y\(_{2}\)O\(_{3}\)) has been widely used as a host material for trivalent rare earth (RE) dopants, or activators, which emit photons in the visible light or the near-infrared (NIR) ranges [1-5]. Its wide band gap (5.5 eV) and low phonon vibrations make yttria a suitable host material for a wide emission range of phosphors. For instances, Eu\(^{3+}\) in infrared (NIR) ranges [1U5]. Its wide band gap (5.5 eV) and low absorption by Bi\(^{3+}\) at NIR wavelengths [5U6].

Activators by the 6\(_p\)\(^2\)\(\rightarrow\)6\(_s\)\(^2\) transition of Bi\(^{3+}\) [6-10]. Bi\(^{3+}\) absorbs two ranges of wavelengths, 325-346 nm and 370-378 nm, at two nonequivalent sites of yttrium, S\(_6\) and C\(_2\) [7-10]. The S\(_6\) and the C\(_2\) sites are known to emit at 410 and 500 nm, photons, respectively.

The RE activators in Bi\(^{3+}\)-doped yttria efficiently absorb photons mostly at 500 nm, which are emitted from the Bi\(^{3+}\) at the C\(_2\) site [7-10]. For a higher efficiency of energy conversion in a Bi\(^{3+}\)-sensitized phosphor, the host lattice should have high crystallinity so that the emission peak from Bi\(^{3+}\) at the C\(_2\) site becomes sharp and intense. In addition, the sensitizer-activator distance should be closer because the energy transfer efficiency \(\eta_{\text{eff}}\) follows the relation, \(\eta_{\text{eff}} \propto 1/R_{\text{SA}}^2\), where \(R_{\text{SA}}\) is the sensitizer-activator distance. Therefore, the PL intensity increases with the doping concentration of the RE activator up to a certain limit.

Recently, combustion techniques and colloidal methods have been used to synthesize yttria nanophosphors [11-13]. These methods are followed by high-temperature annealing (~1300 K) for increasing the crystallinity and removing the radicals. For Y\(_{2}\)O\(_{3}\):Bi\(^{3+}\) synthesis, the former method is more frequently
employed. The optimized Bi mole percentage that gives the best PL intensity and peak broadness by Bi$^{3+}$ at the S$_6$ and the C$_2$ sites is heavily influenced by several fabrication conditions [10-14]. For example, Jacobsohn et al. reported that the type of combustion fuel affects the PL properties; in particular, they showed that urea as the fuel gives the best peak sharpness with equal intensities from Bi$^{3+}$ at the S$_6$ and the C$_2$ sites [14]. The work of Huang [10], which used longer annealing time, however, showed a weaker and a broader PL peak from Bi$^{3+}$ at the C$_2$ site than that from the S$_6$ site, despite the use of identical chemical starting materials and fuels as for the study of Jacobsohn.

The origins of this discrepancy in the optical properties mostly fall into two cases: the formation of a variety of phases or the introduction of native defects. It is reasonable to exclude the formation of a variety of phases for Y$_2$O$_3$:Bi$^{3+}$ synthesis because X-ray diffraction (XRD) measurements demonstrated the uniform bixbyite structure after an annealing process [7-11, 14]. Therefore, native defects and defect doping with H, C or N atoms can exist and influence the optical properties of the crystals, as can be seen in other phosphor materials that have been well-studied theoretically, such as GaN and ZnO [15-19]. However, the conditions of the heat treatments also significantly alter the peak broadness and intensity; hence, the roles of the native defects are important in the Y$_2$O$_3$:Bi$^{3+}$ system.

We theoretically investigated the formation of native point defects in Y$_2$O$_3$:Bi$^{3+}$ in the experimentally employed conditions for the annealing temperature and the oxygen pressure, as well as their roles in the PL properties. Based on the defect energy levels, we predicted the absorption wavelengths of each defect system. Our defect modeling includes dopant-defect complexes to thoroughly investigate the effects of doped Bi on the energetic stability and the energy levels of point defects. In addition, we prepared Y$_2$O$_3$:Bi$^{3+}$ phosphors under oxygen-poor, ambient, and oxygen-rich conditions and compared their PL intensities. The result showed the good agreement between the theoretical predictions and experimental outputs.

**Calculation methods**

We performed density functional theory (DFT) calculations within the generalized gradient approximation (GGA), with Perdew-Burke-Ernzerhof (PBE) parameterization [25, 26]. We used the VASP software [21], and atomic nuclei and core electrons were described by a projector-augmented wave (PAW) [24]. Khon-Sham orbitals were expanded with a cutoff energy of 450 eV, and a 3×3×3 equally spaced k-point grid was used for the Brillouin zone sampling. A Hubbard U approximation ($U_{sd} = 6$ eV) term [27] was included to correct the splitting of the 5$d$ orbital of yttrium, and the spin-orbit coupling (SOC) was included for the correct description of the bismuth orbitals. With the SOC term, our calculations agreed well with the experimental observations of the 6s and the 6p states of bismuth [6-12]. In the formation energy calculations, the experimental binding energy of an oxygen molecule, 2.56 eV/atom, was employed instead of the GGA value, which is known to significantly overestimate the bonding energy of O$_2$ molecule [28]. The yttria unit cell contains 32 yttrium atoms (8 at the S$_6$ sites and 24 at the C$_2$ sites) and 48 oxygen atoms, as presented in Fig. 1. The cell volume and all atoms were fully relaxed. The Bi$^{3+}$-doped Y$_2$O$_3$ was modeled with the incorporation of one Bi$^{3+}$ ion at an interstitial site (Bi$_i$) or at two yttrium sites, S$_6$ and C$_2$.

**Results and Discussions**

**a. Formation energies and electronic structures of Y$_2$O$_3$ and Y$_2$O$_3$:Bi**

The formation energy of yttria ($\Delta E_{\text{Y}_2\text{O}_3}^f$) was calculated using the equation,

$$\Delta E_{\text{Y}_2\text{O}_3}^f = E_{\text{Y}_2\text{O}_3} - 2E_{\text{Y}} - \frac{3}{2}E_{\text{O}_2},$$

where $E_{\text{Y}_2\text{O}_3}$, $E_{\text{Y}}$, and $E_{\text{O}_2}$ are the total energies of the yttria crystal, solid yttrium, and an isolated oxygen molecule, respectively. The formation energy ($\Delta E_{\text{Y}_2\text{O}_3}^f$), the lattice constant and the band gap of yttria are presented in Table I, along with a comparison to the values from a previous DFT study [23] performed using the GGA functional of Perdew-Wang (PW91) [21] and an experimental study [29]. The formation energy and the lattice constant from the PBE calculations are very close to the experimental values, as is shown in Table I. The band gap was underestimated in the PBE calculations, whereas it was corrected to nearly the experimental value by inclusion of U ($U_{sd} = 6$ eV). The SOC term gives negligible changes in the band gap of yttria.

The free energy of Bi-doping was calculated using the chemical reactions below (reactions I, II and III). Temperatures of 800 and 1300 K were considered because combustion and annealing were performed at these temperatures in many reported experiments [7-10]. The solid and liquid phases of bismuth oxide (Bi$_2$O$_3$) were considered as references for the bismuth chemical potential for 800 and 1300 K, respectively, because the melting point is 1100 K [11, 14].
Substitution of Y:

$$\left(1 - \frac{1}{2}x\right)Y_2O_3 + \frac{x}{2}Bi_2O_3 + \Delta G^{f}_{Y_2O_3} \leftrightarrow Y_{2-x}Bi_xO_3.$$  \hspace{1cm} (I)

Substitution of O (anti-site):

$$Y_2O_3 + \frac{x}{2}Bi_2O_3 + \Delta G^{f}_{Y_2O_3,Bi} \leftrightarrow Y_{2-x}Bi_xO_3 + \frac{5x}{4}O_{2(g)}.$$  \hspace{1cm} (II)

Bi interstitial:

$$Y_2O_3 + \frac{x}{2}Bi_2O_3 + \Delta G^{f}_{Y_2O_3,Bi} \leftrightarrow Y_{2-x}Bi_xO_3 + \frac{3x}{4}O_{2(g)}.$$  \hspace{1cm} (III)

The Bi-doping energy ($\Delta G^{f}_{Y_2O_3,Bi}$) is the change in the free energy by Bi-doping per Bi atom. In our calculations of $\Delta G^{f}_{Y_2O_3,Bi}$, the thermal energies of the solids ($Y_2O_3$,$Bi$, $Y_2O_3$, and $Bi_2O_3$) were ignored because their contributions to $\Delta G^{f}_{Y_2O_3,Bi}$ would be largely cancelled out. Hence, the Gibbs free energies can be replaced by the calculated total energies of $Y_2O_3$,$Bi$, and $Y_2O_3$. The calculated $\Delta G^{f}_{Y_2O_3,Bi}$ under extremely oxidizing and reducing conditions at 298 K are listed in Table II. The upper limit of the oxygen chemical potential, which is under extremely oxidizing conditions, is given by:

$$\mu_O \leq \mu_O^0 = \frac{1}{2} E_{O_2}.$$  \hspace{1cm} (2)

The lower limit can be defined when yttria is decomposed into solid yttrium and oxygen gas. Thus, $\mu_O = \mu_O^0 = E_Y$ under extremely reducing conditions, where $E_Y$ is the total energy of yttrium in the solid phase. The chemical potential of oxygen was calculated using the thermodynamic equation for ideal gases and the chemical potential at standard temperature and pressure. As the reference point, $\mu_O^0$ is used as the zero point:

$$\Delta \mu_O = \mu_O - \mu_O^0.$$  \hspace{1cm} (3)

The oxygen chemical potential was expressed as:

$$\Delta \mu_O(T, P_{O_2}) = \frac{1}{2} [\bar{\mu}_{O_2}(T, P^0) + k_B T \ln(P_{O_2}/P^0)],$$  \hspace{1cm} (4)

where $\bar{\mu}_{O_2}(T, P^0)$ is the $O_2$ chemical potential at standard pressure ($P^0$) and temperature $T$ [30].

The Bi-doping energy ($\Delta G^{f}_{Y_2O_3,Bi}$) of the reactions considered are in Table II and are plotted in Fig. 2 for the two representative temperatures of 800 K and 1300 K with varying oxygen pressures. The experimental heat of fusion of $Bi_2O_3$, 6.8 kcal/mole (0.30 eV/f.u.) [31], which is higher than the melting temperature of $Bi_2O_3$, was added to the formation energy for calculations at 1300 K. Our calculations show that substitutional $Bi^{3+}$ doping at the $S_b$ site is the more favorable, than at the $C_2$ site by the energy difference of 0.08eV. The preference of $Bi^{3+}$ at $S_b$ is well consistent with the tendency found in the Stanek’s simulation work using Buckingham potentials: a dopant with larger ionic radius than host cation favors the $S_b$ site of an oxide in bixbyite structure [32]. $Bi$ as an interstitial or an anti-site defect is very high in energy at atmospheric conditions. Obeying the Boltzmann factor,
Table II. Bi doping energies at 298 K and the corresponding lattice constants.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Charge on defect (e)</th>
<th>Formation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_O )</td>
<td>0</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>-4.05</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>-7.76</td>
</tr>
<tr>
<td>( V_{S6} )</td>
<td>0</td>
<td>13.59</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>14.58</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>15.88</td>
</tr>
<tr>
<td></td>
<td>-3</td>
<td>17.31</td>
</tr>
<tr>
<td>( V_{C2} )</td>
<td>0</td>
<td>13.71</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>14.80</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>16.21</td>
</tr>
<tr>
<td></td>
<td>-3</td>
<td>19.34</td>
</tr>
<tr>
<td>Pure ( Y_2O_3 )</td>
<td>0</td>
<td>7.70</td>
</tr>
<tr>
<td>( O_i )</td>
<td>-1</td>
<td>9.33</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>11.19</td>
</tr>
<tr>
<td>( Y_i )</td>
<td>0</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>-0.70</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>-5.36</td>
</tr>
<tr>
<td></td>
<td>+3</td>
<td>-8.95</td>
</tr>
<tr>
<td>( O_{C2} )</td>
<td>0</td>
<td>18.24</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>20.04</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>23.12</td>
</tr>
<tr>
<td>( Y_O )</td>
<td>0</td>
<td>5.86</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>-4.68</td>
</tr>
<tr>
<td></td>
<td>+3</td>
<td>-9.39</td>
</tr>
<tr>
<td>( V_O-Bi_{S6} )</td>
<td>0</td>
<td>6.57</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>-4.88</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>-7.86</td>
</tr>
<tr>
<td>( V_O-Bi_{C2} )</td>
<td>0</td>
<td>6.67</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>-4.58</td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>-5.11</td>
</tr>
<tr>
<td>( O_i-Bi_{S6} )</td>
<td>0</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>8.54</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>11.20</td>
</tr>
<tr>
<td>( O_i-Bi_{C2} )</td>
<td>0</td>
<td>6.46</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>8.31</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>10.89</td>
</tr>
</tbody>
</table>

Table III. Point defect formation energies in bixbyte \( Y_2O_3 \) under extremely reducing (\( \mu_V = \mu_V^0 \)) and oxidizing (\( \mu_O = \mu_O^0 \)) conditions, the upper limits of eqn. (5) and (6). \( V_O-Bi_{S6} \) is an O vacancy in the

The localized 6s- and 6p-orbitals of \( Bi^{3+} \) appear very clearly in the electron density of states (DOS) in Fig. 3. The separation of the 6s- and the 6p-orbitals was not described well without the SOC. The \( Bi^{3+} \) at both the \( S_6 \) and the \( C_2 \) sites has sharply localized 6s-(occupied) and 6p- (unoccupied) orbitals within the band gap of the yttria host. The calculated energy distances between the in-gap 6s- and 6p-orbitals are 3.10 (400 nm) and 3.42 eV (362 nm) for the \( S_6 \) and the \( C_2 \) sites, respectively. The wavelengths of excitation correspond to the 6s-6p separations, which lead to the \( ^1S_0 \rightarrow ^1P_1 \) transitions being slightly longer than the experimental measurements, 378 nm and 325 nm. One common method to correct the energy levels for an underestimated band gap is to rigidly shift the occupied states and the unoccupied states as much as the gap under estimation, while fixing the level intervals between the occupied states and between the unoccupied states. With this method, the corrected \( ^1S_0 \rightarrow ^1P_1 \) transition wavelengths of \( Bi^{3+} \) at the \( S_6 \) and the \( C_2 \) sites are 376 and 342 nm, respectively, which agrees very well with the experiments.

The calculated Bi doping energy (\( \Delta G_{Y_2O_3:Bi}^f \)) as a function of \( P_{O_2} \) at 800 K and 1300 K. Anti-site (\( Bi_{O} \)) doping becomes dominant below \( P_{O_2} = 4.0 \times 10^{20} \) atm at 800 K and \( P_{O_2} = 2.5 \times 10^{20} \) atm at 1300 K. The calculated Bi doping energy (\( \Delta G_{Y_2O_3:Bi}^f \)) as a function of \( P_{O_2} \) at 800 K and 1300 K. Anti-site (\( Bi_{O} \)) doping becomes dominant below \( P_{O_2} = 4.0 \times 10^{20} \) atm at 800 K and \( P_{O_2} = 2.5 \times 10^{20} \) atm at 1300 K.
vicinity of Bi$^{3+}$ at the S$^6$ site, and the other notations were made in the same way.

Because the photoexcitation by Bi$^{3+}$ occurs between the states within the band gap of the host material, the sensitized luminescence of Y$_2$O$_3$:Bi$^{3+}$-RE does not follow the theoretical scheme of Mott and Gurney [33], in which the electrons and holes recombine at the activator ions. The energy transfer with a 500 nm photon emitted from Bi$^{3+}$ at the C$_2$ site mainly contributes to the sensitization.

**Fig. 4.** Defect formation energy for $P_{O_2} = 0.21$ atm, O-rich and O-poor limits at (a) 300 K and (b) 1300 K, as a function of Fermi level in the gap of yttria. Slopes of each line are the charges of the defects. Solid and dashed lines are the formation energies for pure and Bi$^{3+}$-doped Y$_2$O$_3$.

**b. Defect formations in Y$_2$O$_3$ and Y$_2$O$_3$:Bi**

We calculated the point defect formation energies of Y$_2$O$_3$ and Y$_2$O$_3$:Bi$^{3+}$ within the chemical potential ranges of Y and O, given by:

$$\mu_0^v + \frac{1}{2} \Delta E_{V_{Y_2O_3}}^v < \mu_Y \leq \mu_0^v$$

(5)

We considered the native point defects of pure Y$_2$O$_3$ to be oxygen vacancies ($V_O$), yttrium vacancies at the S$_6$ ($V_{S6}$) and the C$_2$ ($V_{C2}$) sites and interstitial oxygen ($O_i$) and yttrium ($Y_i$). In addition, we also included the complexes of each point defect and bismuth at the nearest distance, to investigate the affinity of point defects for the bismuth dopant, which may change the defect concentrations and electronic structures. We also considered the defect to be charged.
Equation (7) gives the defect formation energies of point defects with a charge \( q \) \( \Delta E_f(q) \), as a function of the Fermi level, using the equation:

\[
\Delta E_f(q) = E[D^q] + \mu_i - E^0 + q(E_v + \Delta V + \varepsilon_F),
\]

where \( E[D^q] \) is the total energy of the defect-containing \( \text{Y}_2\text{O}_3 \) (\( \text{Y}_2\text{O}_3;\text{Bi}^{3+} \)) cell with a charge \( q \), \( E^0 \) is the total energy of the defect-free \( \text{Y}_2\text{O}_3 \) \( (\text{Y}_2\text{O}_3;\text{Bi}^{3+}) \), \( \mu_i \) is the chemical potential of the element \( i \) added to (removed from) the \( \text{Y}_2\text{O}_3 \) \( (\text{Y}_2\text{O}_3;\text{Bi}^{3+}) \) cell to generate a point defect, \( E_v \) is the valence band maximum (VBM) of the defect-free \( \text{Y}_2\text{O}_3 \), \( \Delta V \) is the shift in the VBM in the defective cell by a point defect, relative to that in the defect-free \( \text{Y}_2\text{O}_3 \), and \( \varepsilon_F \) is the Fermi level referenced to \( E_v \).

The calculated formation energies of the point defects of yttria under extremely oxidizing (\( \mu_{O_2} = \mu_{O_2}^0 \)) and reducing (\( \mu_{O_2} = \mu_{O_2}^- \)) conditions, when the Fermi level is at the VBM, are listed in Table III. Between the two types of interstitial sites in the bixbyite structure, site 8a with six oxygen and six yttrium atoms at its neighbors and site 16c with six oxygen and four yttrium atoms at its neighbors, site 16c is preferred by both the yttrium and the oxygen atoms. We compared the energetic stabilities of the point defects in the pure yttria and the adjacent sites to the doped Bi atom in \( \text{Y}_2\text{O}_3;\text{Bi}^{3+} \). Among the point defects considered in this study, only \( \text{V}_{O_2}^- \) and \( \text{O}_{2}^+ \) prefer to be in the vicinity of the doped Bi atom at the \( S_6 \) and the \( C_2 \) sites, respectively. Other point defects have a higher formation energy than those in the pure yttria.

The pure yttria at room temperature \( (T = 300 \text{ K}) \) \( (\text{Fig. 4(a)}) \) has the same dominant defects under O-rich conditions and at atmospheric oxygen pressure \( (P_{O_2} = 0.21 \text{ atm}) \): the \( \text{V}_{O_2}^- \) defect in the \( p \)-type region and \( \text{O}_{2}^+ \) and \( \text{O}_{2}^- \) in the \( n \)-type region. In the O-poor limit at 300 K for pure \( \text{Y}_2\text{O}_3 \), the defects \( \text{Y}_{3}^{2+}, \text{O}_{2}^+ \) and \( \text{O}_{2}^- \) are competing in the \( p \)-type region, and the \( \text{V}_{O_2}^+, \text{V}_{O_2}^0 \) and \( \text{V}_{O_2}^- \) defects become the dominant defects as it becomes \( n \)-type, following the reaction formula:

\[
\text{Y}_{3}^{2+} + \frac{3}{2} \text{O}_{2}^- = \text{Y}_{3}^{3+} + \text{V}_{O_2}^0 + \frac{3}{4} \text{O}_2(g) \quad (\text{IV})
\]

\[
\text{Y}_{3}^{2+} + \frac{3}{2} \text{O}_{2}^- = \text{Y}_{3}^{3+} + \text{V}_{O_2}^0 + \frac{3}{2} \text{V}_{O_2}^2 + 3 \text{e}^- + \frac{3}{4} \text{O}_2(g) \quad (\text{V}).
\]

At heat treatment temperature and atmosphere \( (T = 1300 \text{ K}, P_{O_2}=0.21 \text{ atm}) \), the dominant point defects in the pure and the Bi-doped yttria are the oxygen Frenkel pair \( (\text{V}_{O_2}^0 \text{and} \text{O}_{2}^-) \), as Fermi level is pinned at the intersection of the \( \text{Bi}_{2}\text{O}_{3};\text{V}_{O_2}^0 \) and the \( \text{Bi}_{2}\text{O}_{3};\text{O}_{2}^- \) curves. The concentrations of the defect pairs in pure and 1%Bi-doped yttria are \( 1.31\times10^{23} \text{cm}^{-3} \) and \( 3.19\times10^{23} \text{cm}^{-3} \), respectively, according to the equation,

\[
[V_{O_2}^0] = [O_{2}^-] = \exp \left[ \frac{\Delta E_f(q)}{k_B T} \right],
\]

where \([V_{O_2}^0] \) and \([O_{2}^-] \) are the concentrations, and \( \Delta E_f(q) \) is the defect formation energy of each defect obtained at the pinned Fermi level \( (\text{Fig. 4(b)}) \).

In O-poor limit at \( T = 1300 \text{ K} \), the Bi-doped \( \text{Y}_2\text{O}_3 \) also has \( \text{Y}_{O_2}^{3+} \) due to the temperature effect. We attribute the lower formation energies of oxygen vacancies in the vicinity of the \( \text{Bi}_{3}^{3+} \) dopant to the longer Bi-O bond lengths than those of Y-O. The bond lengths of Bi-O and Y-O obtained from PBE schemes show same tendency with those from the \textit{ab initio} embedded cluster methods [34]: the bond lengths of Bi-O and Y-O at \( S_6 \) are larger than two of those at \( C_2 \) site and smaller than the last one (Table IV). The PBE method gives bond lengths and lattice constants, which are closer to the experimental values (See Table I). As is discussed in the next section, much higher concentrations of \( \text{V}_{O_2}^0 \) and \( \text{O}_{2}^- \) Frenkel defect pairs in \( \text{Y}_2\text{O}_3;\text{Bi}^{3+} \) might remarkably change the optical properties of the system during the high temperature treatment.

<table>
<thead>
<tr>
<th>Cation site</th>
<th>Cation Element</th>
<th>d1 (Å)</th>
<th>d2 (Å)</th>
<th>d3 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6</td>
<td>Y</td>
<td>2.285</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S6</td>
<td>Bi</td>
<td>2.370</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>Y</td>
<td>2.246</td>
<td>2.263</td>
<td>2.343</td>
</tr>
<tr>
<td>C2</td>
<td>Bi</td>
<td>2.299</td>
<td>2.362</td>
<td>2.445</td>
</tr>
</tbody>
</table>

Table IV. Calculated bond lengths between cations (Y, Bi) and oxygen in \( \text{Y}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3;\text{Bi}^{3+} \). The notation \( d_1, d_2 \) and \( d_3 \) are the cation-anion distances in sequences.

c. Effects of point defects on the electronic structures and optical properties of \( \text{Y}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3;\text{Bi}^{3+} \)

We present the electron density of states (DOS) for the defect-containing yttria in Fig. 5. The neutral \( (\text{V}_{O_2}^0) \) and the singly charged oxygen vacancies \( (\text{V}_{O_2}^-) \) in the yttria induce deep donor-like levels. The doubly charged oxygen vacancy \( (\text{V}_{O_2}^{3-}) \) induces a deep unoccupied state in the middle of the yttria band gap. The \( \text{O}_{2}^- \) defect induces occupied levels near the VBM, which are filled by oxygen 2p electrons. The expected photon energy absorbed by the \( \text{Y}_{O_2}^{3+} \) from the positions of the Fermi level and the induced in-gap states from the calculated DOS is 4.5 eV, which is expected to have an effect on the energy transfer or the emission from the \( \text{Bi}_{3}^{3+} \) dopant. On the other hand, \( \text{Y}_{O_2}^{3+} \) has donor-like states in the gap and also induces the level to coordinate strongly to four yttrium atoms (one \( S_6 \) and three \( C_2 \) sites). One of the expected photoexcitation energies from the \( \text{Y}_{O_2}^{3+} \) is at approximately 1.2 eV, which is fatal for the NIR emitting phosphor. Note that the discussion for the defects in yttria can be applied to the same type of defects in the \( \text{Y}_2\text{O}_3;\text{Bi}^{3+} \) system when the sites are far away from the bismuth atoms.
Because a good phosphor should not absorb the emitted light from the dopants and waste the photon energy, we tested whether the two major defects of $O^{2-}$ and $V_{O}^{2+}$ absorb emitted photons from the bismuth dopants. We found that $O^{2-}$ in the vicinity of $Bi^{3+}$ at $C_2$ site absorbs photon energy of 4.08 eV (304 nm), which is much higher energy than emission from $Bi^{3+}$. On the other hand, $V_{O}^{2+}$ in the vicinity of $S_6$ site can absorb the emission from $Bi^{3+}$ at $C_2$ site such that it degrades the performance of the phosphor. $Bi^{3+}$ at the $C_2$ site emits around 500 nm wavelength photons [5-10]. As is drawn in Fig. 6, $V_{O}^{2+}$ absorbs 473 nm and 492 nm photons, which are similar in wavelength to the emitted photon from $Bi^{3+}$. On the other hand, $O^{2-}$ does not absorb such photons (Fig. 6(c)), and thus, an oxygen interstitial will not cause harm to the PL properties of the phosphor.

The dominant point defects of $Y_2O_3;Bi^{3+}$ annealed at high temperature have long been in question. Our DFT calculations predict that the dominant point defects are the Frenkel pair of $V_{O}^{2+}$ and $O^{2-}$, with concentrations of $3.19 \times 10^{16}$ cm$^{-3}$ for 1% Bi doping, which is dense enough to significantly affect the optical properties [35, 36]. From the calculated defect formation energies and the absorption wavelength of defect sites, we found that the $Bi^{3+}$ doping increases the concentration of $V_{O}^{2+}$ defects which absorb the significant amount of photons emitted not only from $Bi^{3+}$ at the $S_6$ site, where $V_{O}^{2+}$ is located, but also from $Bi^{3+}$ at the $C_2$ site. Thus, we expect that annealing under oxygen-rich conditions is effective for achieving high emission intensity from $Bi^{3+}$ in the $Y_2O_3$ host, by preventing $V_{O}^{2+}$ formation. Our prediction is well proven by the experimental results obtained with $Y_2O_3;Bi^{3+}$ phosphors prepared under different environments in the next section.

d. Effect of annealing atmosphere on the photoluminescence of $Y_2O_3;Bi^{3+}$

![Fig. 5. Electron DOS for defect-containing $Y_2O_3$. The black dotted lines are the DOS of the total system containing a point defect, normalized by the number of atoms. The blue solid curves are the DOS of the defect atoms. The arrows point to the highest occupied states.](image1)

![Fig. 6. Electron DOS of defective $Y_2O_3;Bi^{3+}$. The black dotted lines are the DOS of the total system normalized by the number of atoms; green and red solid lines are the DOS of 6s and 6p orbitals of doped $Bi^{3+}$; solid orange line is DOS of the interstitial oxygen.](image2)

![Fig 7. PL and PLE patterns of $Y_2O_3;Bi^{3+}$ prepared under ambient atmosphere.](image3)
As it mentioned earlier, several different groups applied the combustion method to obtain $\text{Y}_2\text{O}_3$:Bi$^{3+}$ nanophosphors. Jacobsohn et al., in particular, monitored the heat of combustion of different fuels and found that the emission properties of Bi are significantly influenced by fuels [14]. However, the heating atmosphere has not yet been monitored as a variable. Therefore we followed the combustion method reported by Jacobsohn et al. to make $\text{Y}_2\text{O}_3$:Bi$^{3+}$ and varied the annealing atmosphere to apply our prediction to the real synthetic condition. We prepared 1% Bi-doped $\text{Y}_2\text{O}_3$:Bi$^{3+}$ phosphors and annealed them at 1200 °C for 2 h under ambient condition, oxygen-rich ($\text{O}_2$, >99.9%, 1 atm) and oxygen-poor atmosphere ($\text{N}_2$, >99.9%, 1 atm), respectively. $\text{Y}_2\text{O}_3$:Bi$^{3+}$ prepared under ambient condition showed a very similar PL and PLE patterns in real synthetic condition. We prepared 1% BiUdoped Y$\text{O}_3$:Bi$^{3+}$ nanophosphors. Jacobsohn et al. (Fig. 7) [14]. Interestingly, when the annealing atmosphere was changed to oxygen poor, both $S_6$ and $C_2$ emission decreased by ~13% at $\lambda_{\text{max}}$ whereas under oxygen rich condition, their emission increased by ~12% (Fig. 8). The increase of PL intensity can be important because the quantum efficiency of nanophosphors is often considered lower than 20% and hence every small increase counts for the improvement.

**Fig 8.** PL of $S_6$ and $C_2$ sites of $\text{Y}_2\text{O}_3$:Bi$^{3+}$ prepared under ambient, $\text{O}_2$, and $\text{N}_2$ atmosphere, respectively.

**Conclusions**

We systematically investigated the formation of point defects in the $\text{Y}_2\text{O}_3$:Bi$^{3+}$ system and their effects on the optical properties. We demonstrated that the Bi-doped bixbyite yttria phosphor has a higher defect concentration than the pure matrix. Especially at high temperature (e.g., 1300 K) and at ambient pressure, the Frenkel defect pair of oxygen ($\text{V}_0$ and $\text{O}_i$) is dominant in $\text{Y}_2\text{O}_3$:Bi$^{3+}$, with concentrations of $3.19\times10^{16}$ cm$^{-3}$ for 1% Bi doping. The $\text{V}_0^{2+}$ becomes the re-absorption center for the photons emitted from Bi$^{3+}$ at the $C_2$ site, such that it degrades the efficiency of the green emission or the energy transfer from the Bi dopant to the activator atoms. Our experimental PL measurements agree well with our theoretical prediction. Therefore, we suggest a high-temperature treatment under a high-oxygen partial pressure to achieve high efficiency for $\text{Y}_2\text{O}_3$:Bi$^{3+}$ phosphors.

**Acknowledgements**

We thank the support of the KIST internal projects (Grant No. 2E23891 and 2E24630).

**References**


Affiliations

a Center for Computational Science, Korea Institute of Science and Technology, Hwarangro 14 Gil 5, 136-791, Seoul, Korea. Fax: +82 2 958 5451; Tel: + 82 2 958 5491; E-mail: sckim@kist.re.kr 
b Center for Materials Archtecturing, Korea Institute of Science and Technology, Hwarangro 14 Gil 5, 136-791, Seoul, Korea.

<Graphical Abstract>