

Supporting Information

Investigation into Optical Heating and its Applicability as Thermal Sensor Bifunctional Properties of Yb³⁺ Sensitized Tm³⁺ Doped Y₂O₃, YAG and LaAlO₃ Phosphors

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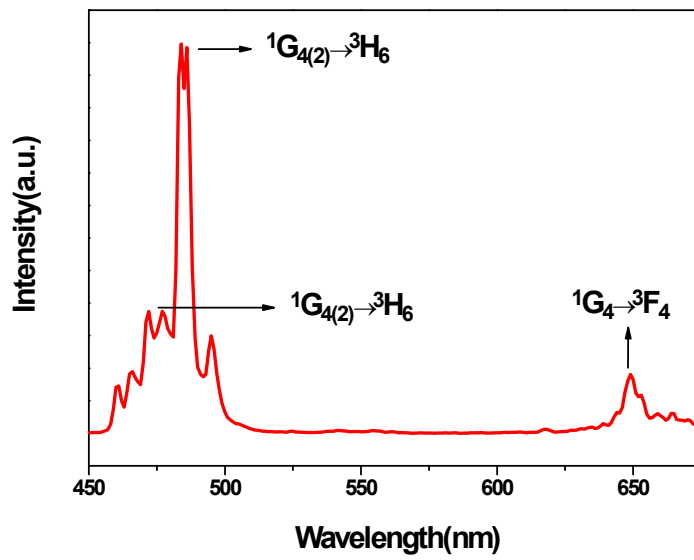


Figure S1 The UC emission spectrum of the $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped YAG phosphor under the excitation of 980 nm diode laser.

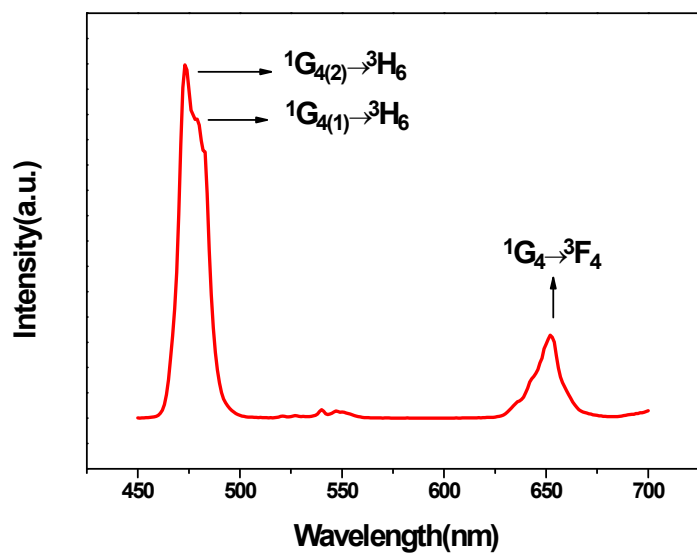


Figure S2 The UC emission spectrum of the Yb³⁺/Tm³⁺ co-doped LaAlO₃ phosphor under the excitation of 980 nm diode laser.

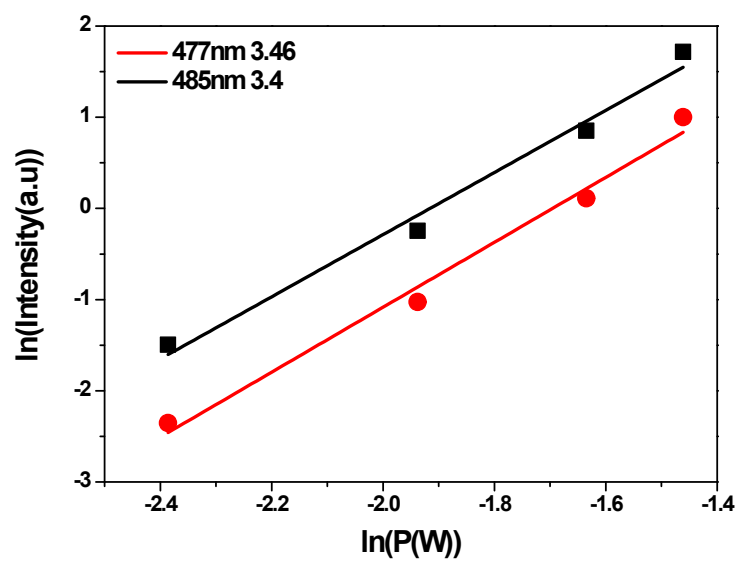


Figure S3 The log-log plots of UC emission intensity of YAG: 0.1%Tm³⁺, 2%Yb³⁺ as a function of a 980 nm laser pumping power.

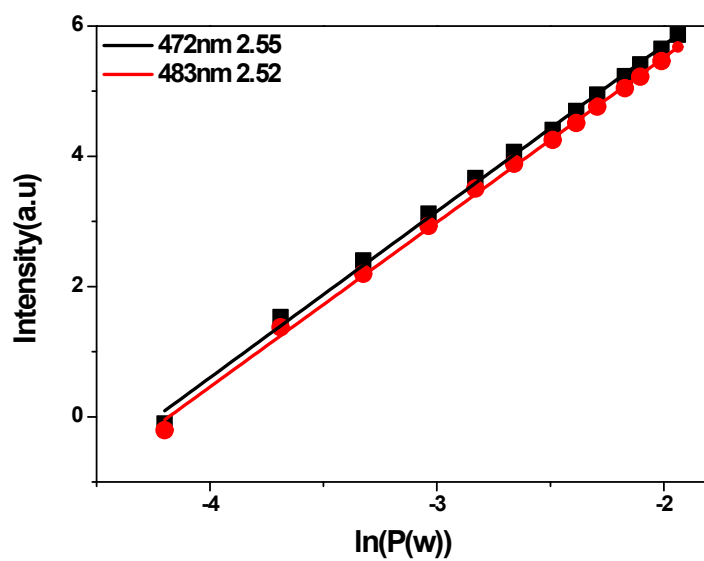


Figure S4 The log-log plots of UC emission intensity of LaAlO₃: 0.1%Tm³⁺, 2%Yb³⁺ as a function of a 980 nm laser pumping power.

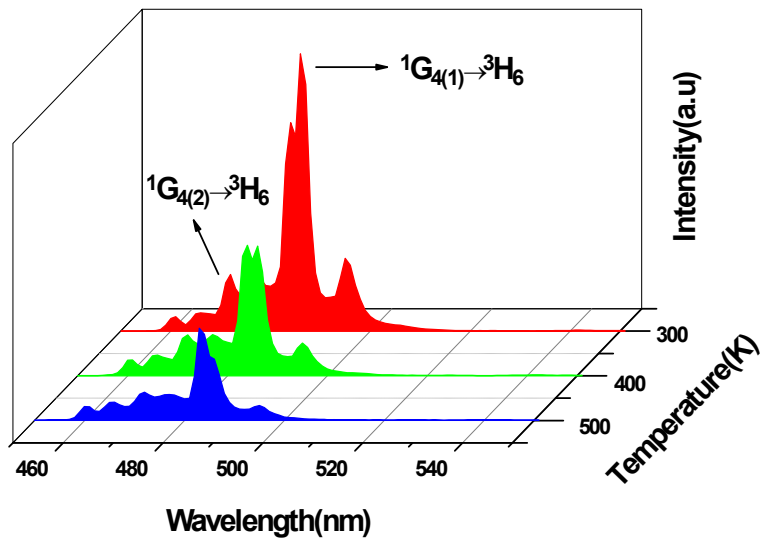


Figure S5 Temperature evolution of the Tm³⁺ blue UC emission spectra excited by 980 nm pump laser for the YAG: 0.1%Tm³⁺, 2% Yb³⁺ phosphor at 300 K, 400 K and 500 K.

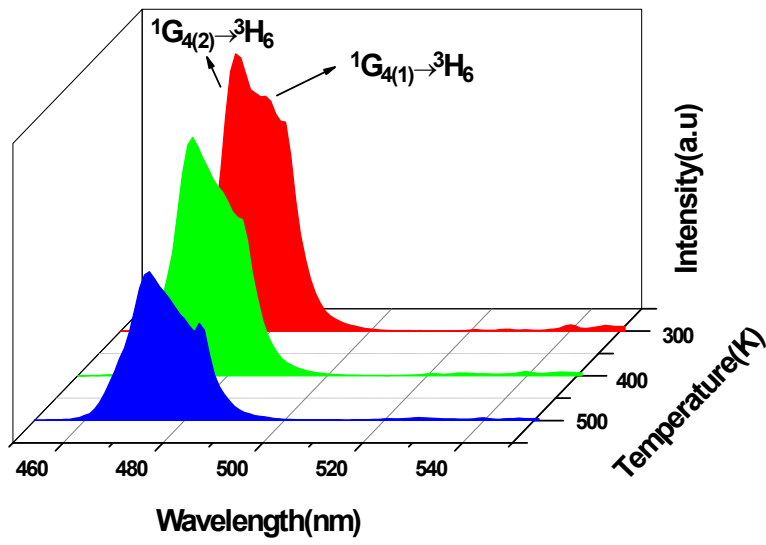


Figure S6 Temperature evolution of the Tm³⁺ blue UC emission spectra excited by 980 nm pump laser for the LaAlO₃: 0.1%Tm³⁺, 2% Yb³⁺ phosphor at 300 K, 400 K and 500 K.

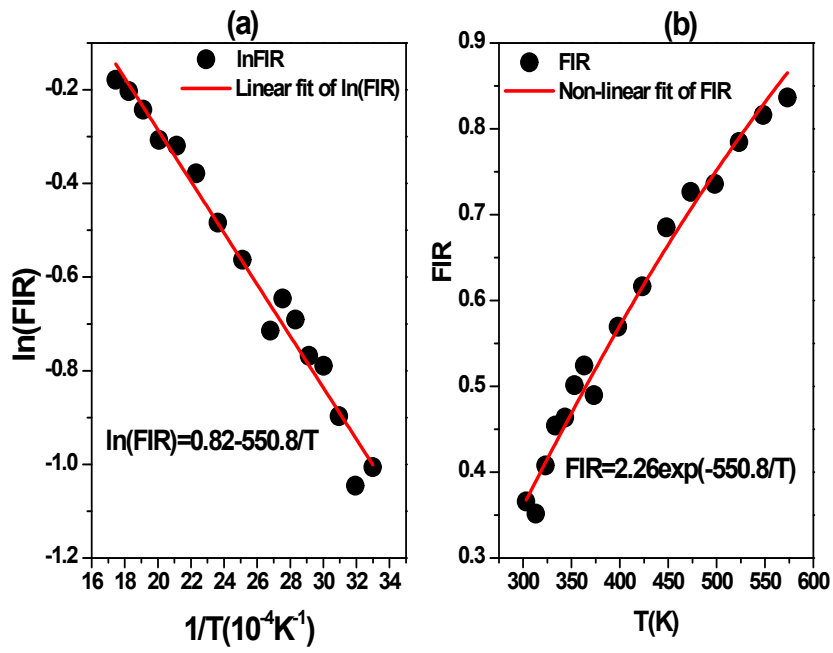


Figure S7 (a) The monolog plot of the FIR versus $1/T$ for the YAG phosphor; (b) FIR (I_{477}/I_{485}) of Tm^{3+} blue UC emissions for the ${}^1\text{G}_{4(2)}/{}^1\text{G}_{4(1)} \rightarrow {}^3\text{H}_6$ transitions as a function of temperature in the range of 303-573 K.

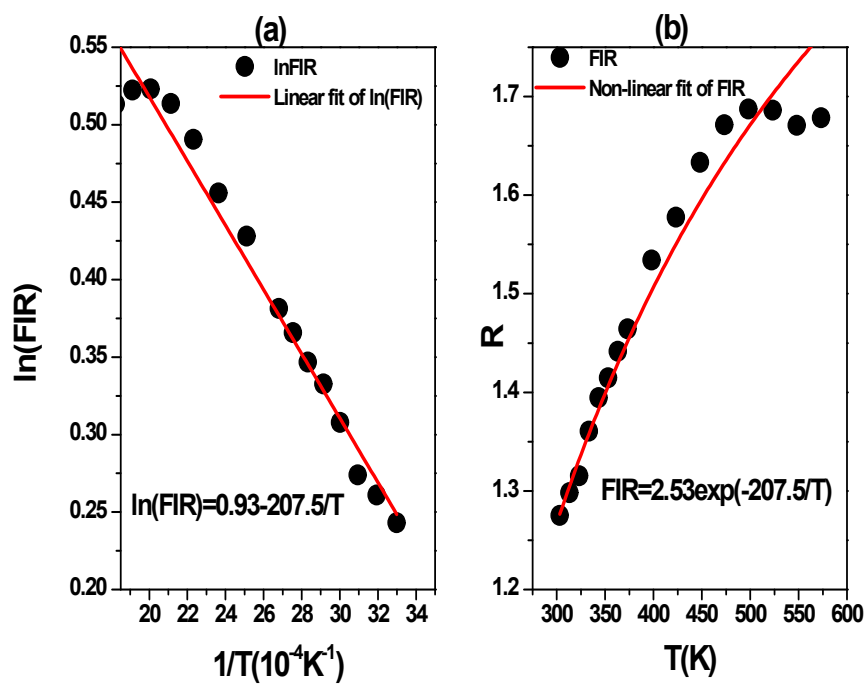


Figure S8 (a) The monolog plot of the FIR versus $1/T$ for the LaAlO_3 phosphor; (b) FIR (I_{472}/I_{483}) of Tm^{3+} blue UC emissions for the ${}^1\text{G}_{4(2)}/{}^1\text{G}_{4(1)} \rightarrow {}^3\text{H}_6$ transitions as a function of temperature in the range of 303-573 K.

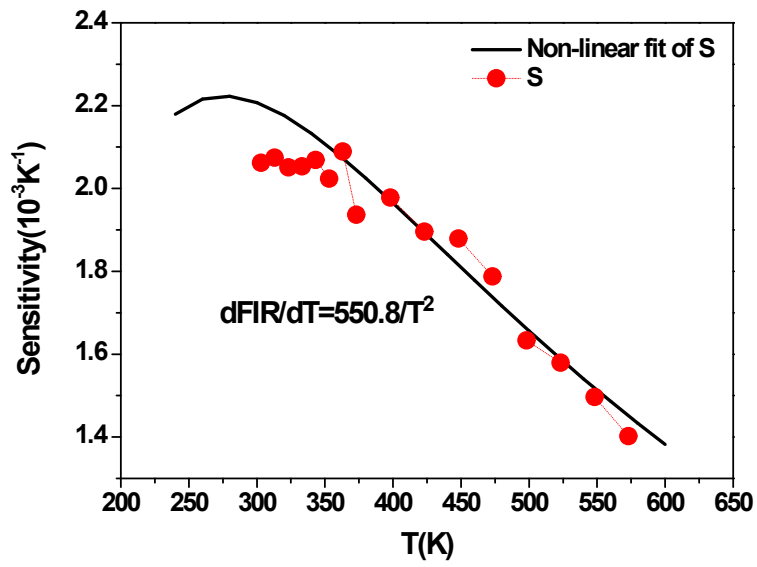


Figure S9 The sensor sensitivity $S = dFIR/dT$ as a function of the temperature for YAG : 0.1%Tm³⁺, 2%Yb³⁺ phosphor.

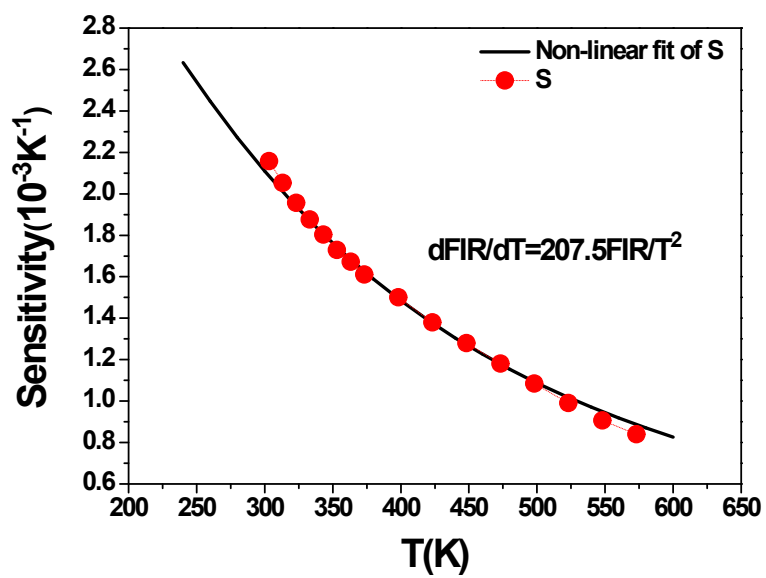


Figure S10 The sensor sensitivity $S = dFIR/dT$ as a function of the temperature for $LaAlO_3 : 0.1\%Tm^{3+}, 2\%Yb^{3+}$ phosphor.

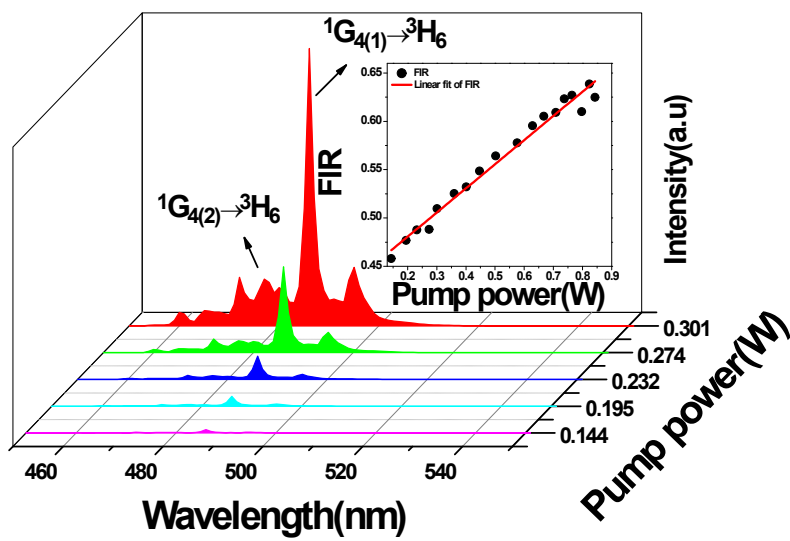


Figure S11 The UCL spectra of the blue bands $^1G_{4(2)}/^1G_{4(1)} \rightarrow ^3H_6$ of Tm^{3+} with different pumping power for YAG: 0.1% Tm^{3+} , 2% Yb^{3+} . Inset: FIR as a function of laser pump power.

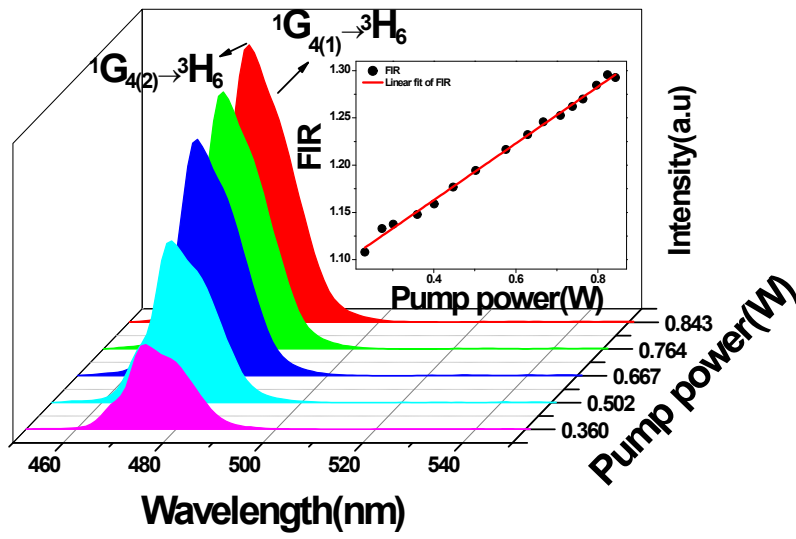


Figure S12 The UCL spectra of the blue bands ${}^1G_{4(2)}/{}^1G_{4(1)} \rightarrow {}^3H_6$ of Tm^{3+} with different pumping power for $\text{LaAlO}_3: 0.1\% \text{Tm}^{3+}, 2\% \text{Yb}^{3+}$. Inset: FIR as a function of laser pump power.

The relationship of chemical bond covalency with the upconversion luminescence as well as temperature sensing property.

The fluorescence intensity ratio of two upconversion emissions, which come from thermally coupled energy levels (TCLs) of rare earth ions, can be written as follows [1-4]:

$$FIR = \frac{I_2}{I_1} = \frac{N_2 A_2 h \nu_2}{N_1 A_1 h \nu_1}, \quad (1)$$

where I_2 and I_1 are the integrated intensities of the transitions of ${}^1G_{4(2)} \rightarrow {}^3H_6$ and ${}^1G_{4(1)} \rightarrow {}^3H_6$, respectively (Tm^{3+}). N_2 and N_1 the corresponding populations, and A_2 and A_1 the spontaneous-emission rates of ${}^1G_{4(2)}$ and ${}^1G_{4(1)}$ states, respectively. The energy gap of ${}^1G_{4(2)}$ and ${}^1G_{4(1)}$ is narrow, resulting in the electrons of ${}^1G_{4(2)}$ level are easily populated to the ${}^1G_{4(1)}$ by thermal excitation. Furthermore, the fluorescence intensity ratio (FIR) of TCLs can be written as follows [5]:

$$FIR = \frac{I_2}{I_1} = \frac{N_2 A_2 h \nu_2}{N_1 A_1 h \nu_1} = \frac{g_2}{g_1} \exp\left(\frac{-\Delta E}{K_B T}\right) \frac{h \nu_2 A_2}{h \nu_1 A_1}, \quad (2)$$

where g_2 , g_1 are the degeneracy $2J+1$ of the ${}^1G_{4(2)}$ and ${}^1G_{4(1)}$ levels, respectively. A_{fi} indicates the radiative transition probability from state f to i state based on Judd-Ofelt theory [6,7] and can be written as follows:

$$A_{fi} = \frac{64\pi^2 e^2 \nu^3}{3h g_f} \frac{(n^2 + 2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_{\lambda} | \langle 4f^N (\alpha CL) J \| U^{(\lambda)} \| 4f^N (\alpha' C' L' J') \rangle |^2, \quad (3)$$

where ν is the energy of transition between the two multiplets, $U^{(\lambda)}$ ($\lambda=2, 4, 6$) denotes the unit tensor operators of rank λ and Ω_{λ} is the J-O intensity parameters. The terms $| \langle 4f^N (\alpha CL) J \| U^{(\lambda)} \| 4f^N (\alpha' C' L' J') \rangle |^2$ represent the reduced matrix elements. In particular, the electric-dipole line strength C is expressed [6-8]:

$$\begin{aligned}
C &= g_i \langle f | \mu | i \rangle^2 = \sum_m \langle f | \mu | i, m \rangle^2 \\
&= \sum_{\lambda=2,4,6} \Omega_\lambda \langle 4f^N (\alpha CL) J \| U^{(\lambda)} \| 4f^N (\alpha' C' L' J') \rangle^2.
\end{aligned} \tag{4}$$

Then the FIR of ${}^1G_{4(2)}, {}^1G_{4(1)} \rightarrow {}^3H_6$ transitions of Tm^{3+} can be given that

$$\begin{aligned}
FIR &= \exp\left(\frac{-\Delta E}{K_B T}\right) \frac{\nu_2^4 C_2}{\nu_1^4 C_1} \\
&= \exp\left(\frac{-\Delta E}{K_B T}\right) \frac{\nu_2^4}{\nu_1^4} \left(\frac{\Omega_2 * 0.7158 + \Omega_4 * 0.4138}{0.2225 * \Omega_6} + 0.0927 / 0.2225 \right) \\
&= B \exp\left(\frac{-\Delta E}{K_B T}\right),
\end{aligned} \tag{5}$$

where

$$\begin{aligned}
B &= \frac{\nu_2^4}{\nu_1^4} \left[\frac{\Omega_2 * 0.7158 + \Omega_4 * 0.4138}{0.2225 * \Omega_6} + 0.0927 / 0.2225 \right] \\
&\approx \frac{\Omega_2 * 0.7158 + \Omega_4 * 0.4138}{0.2225 * \Omega_6} + 0.0927 / 0.2225.
\end{aligned} \tag{6}$$

In view of the fact that ν_2^4 / ν_1^4 approaches 1, B is mainly decided by $\Omega_{\lambda=2,4,6}$. Crystal parameter Ω_λ denotes some properties of materials. The Ω_6 parameter depends on the rigidity of the medium in which the ions are situated. The Ω_2 is related to the symmetry. It is sensitive to the change of constituent of materials, because crystal structures, bond lengths and covalency are different and then nephelauxetic effects are not the same. It's more sensitive to the environments than others among J-O parameters. So the B is finally decided by Ω_2 . In fact, the Ω_2 parameter is strongly affected by covalent chemical bonding, which has been studied by Jorgensen and Yang [4, 9]. In other words, the B value is strongly affected by covalent chemical bonding [10-12]. However, they just gave the qualitative dependence of the B value with the covalent chemical bonding.

In fact, the sensor sensitivity can be written as follows:

$$S = \frac{dFIR}{dT} = FIR \left(\frac{\Delta E}{K_B T^2} \right) = B \frac{\Delta E}{K_B T^2} \exp\left(\frac{-\Delta E}{K_B T}\right). \tag{7}$$

Generally, the energy gap ΔE is decided by the even-parity of the crystal field of the

hosts and related to the symmetries of the crystal system. Then the S is mainly determined by B. That is to say, the sensor sensitivity is proportional to the bond covalency, which is discussed in detail in the revised manuscript. According to the chemical bond theory, the covalent f_c and ionic f_i of chemical bond as follows [13]:

$$f_c = \frac{(E_h^\mu)^2}{(E_g^\mu)^2}, \quad (8)$$

$$f_i = \frac{(C^\mu)^2}{(E_g^\mu)^2}. \quad (9)$$

According to the equations (1)-(7) above, it is well known that the sensor sensitivity is related to B, which is strongly affected by covalent chemical bonding f_c . Thus the sensor sensitivity can be judged by analyzing the ligand covalency, which is our goal in this work.

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