Electronic supplementary information

Luminescent quenching nature of Mn⁴⁺ in wide band gap inorganic

compounds

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A. The formation energy of YAG with one or two Mn⁴⁺ ions

The formation energy of Mn⁴⁺ doping YAG can be calculated by the following formula:

$$E_{F}(Mn^{4+}) = \frac{1}{x} [E(YAG:xMn^{4+}) - E(YAG) - x\mu_{Mn} + x\mu_{Al}]$$

where $E(YAG:xMn^{4+})$ represents the energy of YAG with one (x = 1) or two Mn⁴⁺ ions (x = 2). The energy of the perfect YAG is denoted as E(YAG). μ_{Mn} and μ_{Al} are the chemical potential of bulk Mn and Al, respectively. For YAG with one Mn⁴⁺ ion, the formation energy is about 2.09 eV, while one more Mn⁴⁺ ion is introduced, the formation energy for each Mn⁴⁺ ion increases to 2.73 eV, implying that the Mn⁴⁺ ions tend to stay away from other Mn⁴⁺ ions

B. The electronic structures of KTF with two Mn⁴⁺ ions



Figure S1 Computed band structures, total and partial density of states (DOS and PDOS) of KTF with two Mn⁴⁺ ions. The Fermi level is set to be 0 eV.

C. Detailed calculation method about the formation energies of intrinsic defects at the O-poor and O-rich conditions

In the thermodynamic equilibrium, chemical potentials $({}^{\mu}{}_{Al}, {}^{\mu}{}_{Y}$ and ${}^{\mu}{}_{0})$ have the constraints:

$$\mu_{Al} \le \mu_{Al}^{bulk}, \mu_{Y} \le \mu_{Y}^{bulk}, \mu_{0} \le \frac{1}{2}\mu_{0}_{2}$$
(1)
$$3\mu_{Y} + 5\mu_{Al} + 12\mu_{0} = E_{Y_{3}Al_{5}O_{12}}$$
(2)

Furthermore, since neither Al_2O_3 nor Y_2O_3 may precipitate from bulk YAG, the ranges of chemical potentials are subjected to the additional constraints:

$$2\mu_{Al} + 3\mu_0 \le E_{Al_2 O_3}$$
(3)
$$2\mu_Y + 3\mu_0 \le E_{Y_2 O_3}$$
(4)

In these constraints, ${}^{E_{Al_2O_3}}({}^{E_{Y_2O_3}}, {}^{E_{Y_3Al_5O_{12}}})$ is the total energy per formula unit of the bulk Al₂O₃ (Y₂O₃, YAG) crystal. All these equations define the ranges of the chemical potentials.

In the O-poor condition, the chemical potentials of Y and Al must be in balance with the potentials in the bulk Y and Al,

$$\mu_{Al} = \mu_{Al}^{bulk} \text{ and } \mu_Y = \mu_Y^{bulk} \tag{5}$$

So, the chemical potential of O can be obtained from equation (2),

$$\mu_0 = \frac{1}{12} (E_{Y_3 A l_5 0_{12}} - 3\mu_Y - 5\mu_{Al})$$
(6)

In the O-rich condition, the chemical potential of O is in balance with the potentials of O atom in O_2 ,

$$\mu_0 = \frac{1}{2}\mu_{0_2} \tag{7}$$

The chemical potentials of Y can be expressed using μ_{Al} through

$$\mu_{Y} = \frac{1}{3} (E_{Y_{3}Al_{5}O_{12}} - 5\mu_{Al} - 12\mu_{0})$$
(8)

From equation (3), we can obtain the upper limit of μ_{Al}

$$\mu_{Al} \le \frac{1}{2} (E_{Al_2 O_3} - 3\mu_0) \tag{9}$$

The lower limit of μ_{Al} could be obtained through equations (4) and (8)

$$\mu_{Al} \ge \frac{1}{10} (2E_{Y_3Al_5O_{12}} - 3E_{Y_2O_3} - 15\mu_0) \tag{10}$$

So,

$$-11.54 \ eV \le \mu_{Al} \le -11.34 \ eV \tag{11}$$

Since the upper limit and the lower limit are very close to each other, we adopt the middle value of the range as the chemical potential of Al for convenience, which is about 11.44 eV.

D. The formation energies of O_i in YAG at different charge states

The neutral O_i is stable when the Fermi level is below 2.99 eV, while O_i^{2-} is stable

at the Fermi level higher than 3.61 eV. When the Fermi level is between 2.99 eV and 3.61 eV, O_i^- is more stable. So the neutral O_i cannot absorb a hole from the VBM to become O_i^+ in the hole-doping compound, but it can absorb an electron from the CBM to become O_i^- in the electron-doping case (the Fermi level is high).



Figure S2 Calculated formation energies of the interstitial O at different charge states versus the Fermi level. The VBM is taken as the reference.

E. The formation energies of Vo in YAG in different charge states



Figure S3 Calculated formation energies of Vo at different charge states versus the Fermi level.

The VBM is taken as the reference.

F. Computed electronic structures of YAG with V_{Al4} , Li_i , Li_{Al4} , Si_{Al4} , Mg_{Al6} , Na_Y or Ca_Y



Figure S4 Computed band structures, total and partial density of states (DOS and PDOS) of YAG with (a) V_{Al4} , (b)Li_i, (c) Si_{Al4}, (d) Li_{Al4}, (e) Mg_{Al6}, (f) Na_Y and (g) Ca_Y. The Fermi level is set to be

0 eV.

G. The formation energies of Fe in YAG at different charge states

The Fe⁴⁺ is stable when the Fermi level is below 0.26 eV, while Fe²⁺ is stable at the Fermi level higher than 3.64 eV. When the Fermi level is between 0.26 eV and 3.64 eV, Fe³⁺ is more stable. Thus, Fe³⁺ or Fe⁴⁺ may coexist with Mn⁴⁺. Since Fe⁴⁺ is only stable when the Fermi level is extremely low, which can only achieved through heavy hole-type doping, it is difficult to stabilize the Fe ion at +4 state. Thus, only the influence of the Fe³⁺ is considered in this work.



Figure S5 Calculated formation energies of Fe at different charge states versus the Fermi level.

The VBM is taken as the reference.