First-principles study on luminescence properties of Eu-doped defect pyrochlore oxide KNbWO$_6$:H$_2$O:Eu$^{3+}$

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Abstract

Defect pyrochlore oxides have attracted a great interest as promising luminescent materials due to their flexible composition and high electron/hole mobility. In this work, we investigate the structural and electronic properties of lanthanide-doped (Ln) defect pyrochlore oxides KNbWO$_6$·0.125Ln$^{3+}$ by using first-principles calculations. We perform structural optimizations of various defect pyrochlore models and calculate their electronic structures, revealing that hydration has a significant influence on both local symmetry around Eu$^{3+}$ ion and band structures with an alteration of their luminescent behaviour. In the hydrated compounds, the electric-dipole $^5$D$_{0}$$\rightarrow$$^7$F$_2$ transition is found to be partially suppressed by the raised local symmetry, and the water molecules in the compounds can mediate the non-radiative energy transfer between the activator Eu$^{3+}$ ions and the host, resulting in the quenching effect. It turns out that the oxygen vacancies are detrimental to luminescence as they reduce the Eu$^{3+}$ ion in its vicinity to Eu$^{2+}$ ion and also serve as traps for conduction electrons excited by incident light. Our calculations for KNbWO$_6$·0.125Ln$^{3+}$ (Ln = Ce, Pr, Nd, Pm, Sm) support that defect pyrochlore oxide KNbWO$_6$ can also be used as luminescence host for Ln$^{3+}$ ion doping, giving a valuable insight into a variation trend in luminescent properties of these materials at atomic level.

Key words: Pyrochlore, Luminescence, Defect, Electronic structure, First-principles

1. Introduction

During the past half century, lots of luminescent materials have been discovered with numerous applications in many areas, including fluorescent lamp [1], photovoltaics and photocatalyst [2][3][4], bio-imaging [5] and white light applications [6]. In order to improve efficiency, life-time and environmental friendliness, much effort has been devoted to develop advanced luminescent materials like lanthanide (Ln) ion doped oxides ZrO$_2$:Ti$^{3+}$, Tb$^{3+}$, Eu$^{3+}$ [7], silicate nitrdes LaSi$_3$N$_5$:Ce$^{3+}$ [8] and phosphates LaPO$_4$:Eu$^{3+}$ [9]. Among many other inorganic compounds used for luminescence hosts, the hollow crystal structures are desirable for accommodating the Ln ions with large ionic radii. In this sense, several pyrochlore compounds with large channel structure were explored as promising luminescent hosts [10][11][12].

We synthesized the hydrated defect pyrochlore oxide KNbWO$_6$·H$_2$O and identified the luminescence properties by experimental measurements [13][14]. Furthermore, Eu-doped hydrated defect pyrochlore KNbWO$_6$·H$_2$O:Eu$^{3+}$ was prepared by ion exchange under hydrothermal condition [13]. In general, the Eu$^{3+}$ ions are known to exhibit characteristic red emission and to be excited by ultra violet (UV) light, and they are noticeable for symmetry-sensitive emission because of the non-degenerate ground state $^7$F$_0$ and non-overlapping $^{2s+1}L_J$ multiplets. [15] In KNbWO$_6$·H$_2$O:Eu$^{3+}$, the emission spectra with strong peaks at 580, 594 and 612 nm were observed, together with excitation spectra with peaks at 394 and 464 nm. All these peaks in the emission/excitation spectra were identified as corresponding to intra-configurational $f$ $\rightarrow$ $f$ transitions of 4f electrons of Eu$^{3+}$ ion. The emission intensity was found to be the strongest at Eu-doping concentration of $x = 0.131$, and to get much stronger after annealed at 450 °C for 2 h. After annealing, the lifetime of emission also became significantly longer due to the effect of dehydration during annealing, implying that hydration might be a possible reason for luminescence quenching. The dehydration of KNbWO$_6$·H$_2$O:Eu$^{3+}$ was also found to influence on the local symmetry of Eu$^{3+}$ ion, being evidenced from the fact that the intensity of emission peak at 612 nm, originated from the electric-dipole $^5$D$_{0}$$\rightarrow$$^7$F$_2$ transition, was strengthened as much as 10 times after annealing, while the magnetic-dipole $^5$D$_{0}$$\rightarrow$$^7$F$_{1}$ transition spectra at 594 nm got slightly stronger. These results indicate that KNbWO$_6$·H$_2$O can be used as efficient luminescent host. In spite of such experimental findings, no theoretical or computational studies on this material have been found, and thus there is lack of the atomistic insight into its luminescent properties.

The Ln-doped luminescence materials have been subject of many first-principles studies within density functional theory (DFT) framework. In DFT calculations of the Ln-doped materials, where the luminescence properties are governed by transi-
tions between the multi-electronic states of the activator Ln ions involving 4f electrons, the challenge is to consider the 4f electrons explicitly. What is worse, as a single-particle ground-state theory, DFT cannot directly explain the transitions between the multi-electronic states. In fact, excepting the constrained DFT (cDFT) method that can manipulate only the 4f − 5d transition, mainly occurring in the Ce³⁺ and Eu²⁺ ions, with a computation of transition energy and Stokes shift [16] [8] [17], it was found to be almost impossible for DFT calculation to reproduce experimentally observed spectra formed by intra-configurational 4f − 4f transitions. Nevertheless, DFT calculations have been generally accepted to provide sufficiently reliable information for crystalline structure and activator-ligand interaction in the Ln-doped materials, being important for estimating the trend in luminescence property. Moreover, the DFT electronic structures can be used to determine the positions of activator levels relative to the host band edges, which are also important for finding optical host-activator combinations [18]. The effect of defects in host compound on luminescence property can also be investigated with DFT calculations [19] [20].

In this study, we perform the DFT calculations on several models related to the Eu-doped hydrated pyrochlore oxide KNbWO₆·H₂O·xEu to investigate the effects of hydration and defects on its luminescence property at atomic level. The optimized structures of various defect-containing models are determined by structural relaxations and subsequently their electronic structures are calculated, determining the position of 4f levels relative to the host band edges. We discuss the potential use of these compounds as a luminescence host for doping other trivalent Ln ions. In the remaining part of this paper, computational methods are given in Section 2, the results and discussion in Section 3 and the main conclusion in Section 4.

2. Methods

2.1. Structural models

The defect pyrochlore oxides with a chemical formula of AB₂O₆ were known to crystallize in cubic phase with a space group of Fd3m, where the crystalline lattices are composed of corner sharing BO₆ octahedra network with 3D large channels and the A cations are located inside the channels. The unit cell contains eight formula units (72 atoms). In the case of KNbWO₆, the B sites are randomly occupied by Nb and W cations at the same probabilities, while the K cations randomly occupy one of every four equivalent crystallographic A sites. From the BVS analysis, it is found that in the unit cell there are eight separate closed hollow spaces, resembling tetrahedron, inside which each K⁺ ion locates on any one of 4 vertex points, as depicted in Fig. 1. For the B sites, the configuration of Nb and W ions is truly random, and thus we suggested 3 different models distinguished by Nb/W sub-lattice ordering: model1 for disorder, model2 for semi-disorder and model3 for order of Nb and W sublattices.

When hydrating the pyrochlore oxide, the resultant KNbWO₆·H₂O does not change the original crystalline lattice symmetry as the cubic phase with a space group of Fd3m, with a lattice constant of a = 10.5073 Å and 8 formula units (96 atoms) in the unit cell [23]. In this hydrated pyrochlore structure, the water molecules reside inside the hollow spaces and thus the K ions are pushed off the hollow (see Fig. S1(b)). With a random placement of water molecule on any one of four equivalent hollow positions, we also suggested three different models for KNbWO₆·H₂O crystal structure, distinguished by configuration of Nb/W random distribution on the B sites. Meanwhile, for doping structures with the Eu ions, three K⁺ ions should be replaced by one Eu³⁺ ion on the A sites to satisfy the electronic charge neutrality, leading to formation of one doped Eu³⁺ ion and two potassium vacancies V_K. Due to the sufficiently large size of lattice constants exceeding 10 Å and the number of atoms over 80, we can safely use the unit cell in the investigation of doped material rather than using the super cell. Based on the experiment with a small amount of Eu atoms, only one Eu atom was supposed to be exchanged in the unit cell, leading to the compounds with chemical formula of KNbWO₆·0.125Eu³⁺ for non-hydrated pyrochlore oxide and KNbWO₆·H₂O·0.125Eu³⁺ for hydrated one respectively. We suggested three different configurations of Eu exchange for each non-hydrated model and two different configurations for the hydrated model.

2.2. Computational details

All the calculations in this study were carried out by means of pseudopotential plane-wave method within the DFT framework, as implemented in Quantum ESPRESSO (QE) package (version 6.2) [24]. As being available from the GBRV Library [25], the ultra-soft pseudopotentials (USPP) were used to describe the ion-electron interaction. In the structural optimizations, the exchange-correlation interaction between valence electrons was considered by using the Perdew-Burke- Ernzerhof (PBE) functional [26] and its revised version for solids (PBEsol) [27] within generalized gradient approximation (GGA). In addition, the Hubbard U [28] term was taken into account for the d states of Eu (U = 4 eV), Nb and W (U = 3 eV) atoms. The wave functions and electronic densities were expanded by using the plane wave basis sets generated with the cut-off energies of 60 and 500 Ry, respectively. Monkhorst-Pack [29] special k-points for the Brillouin zone integration were set to be (2 × 2 × 2) for the structural optimization. These computational parameters guarantee a total energy accuracy of 5 meV per formula unit. The positions of all atoms and lattice constants were fully relaxed until the atomic forces converge to 0.02 eV/Å.

In the electronic structure calculations including the energy bands and density of states (DOS), we only used the PBEsol functional, since it could give the better result than PBE when compared with the experimental lattice constants. Spin-polarization was considered and the denser k-points of (4 × 4 × 4) were used. For the doped models, the 4f electrons of Eu were explicitly treated as the valence electrons by using USPP from PS Library (version 1.04) [30], where the valence
electron configuration is $5s^26s^25p^64d^{10}5d^{10}5f^{6}$. In such 4$f$ states-explicit calculations, the larger cut-off energies of 90 and 800 Ry were used for the sake of convergence. The other doped models with Ln ions (Ce, Pr, Nd, Pm, Sm) were also investigated by using the same computational parameters to the case of Eu doping.

3. Results and discussion

3.1. Structural property

First, we carried out structural optimization of the unit cells for 3 different KNbWO$_6$ models by using the PBE and PBEsol XC functionals. By comparing with the experimental lattice constant, the result can be used as a check on a validity of the computational parameters and XC functionals. Table 1 presents the obtained lattice constants and volume of the unit cells for the three different models in comparison with the experimental one. We note that when allowing the full relaxation of lattice parameters and atomic positions, the optimized crystal structures deviate from the cubic system as obtaining the different lattice constants of $a \neq b$ or $a \neq c$ or $b \neq c$, which can be thought to be caused by somewhat artificial (random) distribution of the atoms. In this situation, the unit cell volume was also provided to make it easy to do comparison with experiment. It turns out that when compared with the experiment, the PBE functional yielded an overestimation of lattice constants with relative errors of 3.1%, 2.4% and 2.2% for model1, model2 and model3, whereas the PBEsol functional provided a good estimation of lattice constants with much lower relative errors of 0.7%, 0.1% and 0.5% respectively. This indicates that the PBEsol functional is more adequate for the defect pyrochlore oxides than PBE and the computational parameters used in this work are sufficiently reliable to give their accurate material properties. Therefore, only the PBEsol functional will be used in the following calculations.

In order to pick out the most stable model among the three different models, we present their total energy differences with respect to the lowest one in Table 1. The model1, disorder model for Nb/W distribution on the B sites, was found to have the lowest total energy, while the model3, order model for Nb/W sublattices, to have the highest total energy with the total energy differences of 5.21 and 7.03 meV/atom in the PBE and PBEsol calculations respectively. It is worth noting that such tendency in total energy is consistent well with the disorder degree of Nb/W distribution on the B sites and can be associated with a strength of interaction between the K$^+$ cations and the oxygen anions. In fact, as shown in Fig. 1 for the optimized atomistic structures of the unit cells for the three different models, the K$^+$ cations reside at the edge of BVS tetrahedron in the model1, formed by isosurface value of BVS = 1 that displays the hollow spaces for the K$^+$ cations, while in the model3 they locate a little inside the BVS tetrahedron. Therefore, the distance between the K$^+$ cations and the neighboring oxygen anions becomes longer going from the model1 to the model2 and to model3, indicating a weakening of the K–O interaction and thus the stability of compound.

Using the PBEsol functional, we then carried out structural optimization of the unit cells for the hydrated pyrochlore KNbWO$_6$·H$_2$O with 3 different models (model1, 2, 3) and for the Eu-doped pyrochlore KNbWO$_6$·0.125Eu$^{3+}$ with 9 different models (model1-1, 1-2, 1-3, 2-1, , , , 3-3). The obtained lattice constants and total energy differences of all the unit cells are presented in Table S1. Unlike the original pyrochlore oxide, the lowest energy models were found to be based on model2 (semi-disorder model) for the hydrated and

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Table 1: Lattice constant ($a$, $b$, $c$), unit cell volume and total energy differences in three different KNbWO$_6$ models shown in Fig. 1 calculated with PBE and PBEsol XC functionals.

| Model | Lattice constants (Å) | Volume (Å$^3$) | $\Delta E$ (meV/atom) |
|-------|---------------------|----------------|---------------------|
|       | $a$  | $b$  | $c$  |       |       |       |
| PBE   |      |      |      |      |      |      |
| Model1 | 10.44 | 10.51 | 10.44 | 1147.50 | 0.00 |
| Model2 | 10.43 | 10.43 | 10.47 | 1139.72 | 0.09 |
| Model3 | 10.51 | 10.40 | 10.40 | 1137.62 | 5.21 |
| PBEsol |      |      |      |      |      |      |
| Model1 | 10.37 | 10.41 | 10.37 | 1120.46 | 0.00 |
| Model2 | 10.35 | 10.35 | 10.38 | 1113.92 | 2.22 |
| Model3 | 10.38 | 10.32 | 10.32 | 1107.61 | 7.03 |
| Exp.  [31] | a = b = c = 10.36 | 1112.84 | – |

Figure 1: Ball-and-stick view of unit cells optimized by using PBEsol + $U$ method for defect pyrochlore KNbWO$_6$ in three different models, distinguished by random distribution of Nb/W atoms; (a) disorder (model1), (b) semi-disorder (model2) and order (model3) models. Tetrahedron-like polyhedron with light pink colour indicates BVS isosurface at the value of BVS = 1 for K atom.
doped pyrochlore oxide. For the Eu-doped hydrated pyrochlore \( \text{KNbWO}_6 \cdot \text{H}_2\text{O}:0.125\text{Eu}^{3+} \), therefore, we constructed the two different unit cells of \( \text{Eu}^{3+} \) exchange based on the optimized model2 of \( \text{KNbWO}_6 \cdot \text{H}_2\text{O} \) (Table S1). In Table 2 we summarize the optimized lattice constants and unit cell volumes of the energetically most favourable models for the original, hydrated, doped and hydrated-doped pyrochlore compounds, obtained by using the PBEsol functional, in comparison with the available experimental data for unit cell volume. For brevity, we list the optimized lattice constants and unit cell volumes of the stable models for \( \text{KNbWO}_6 \cdot \text{H}_2\text{O} \) and (c) hydrated Eu-doped pyrochlore oxide \( \text{KNbWO}_6 \cdot \text{H}_2\text{O}:0.125\text{Eu}^{3+} \), optimized by using PBEsol + \( U \) method. Tetrahedron-like polyhedron with light pink colour indicates BVS isosurface at the value of BVS = 1 for K atom.

Table 2: Lattice constants (\( a, b, c \)) and unit cell volume of the most stable models for \( \text{KNbWO}_6 \) (denoted as Orig), \( \text{KNbWO}_6 \cdot \text{H}_2\text{O} \) (Hyd), \( \text{KNbWO}_6 \cdot 0.125\text{Eu}^{3+} \) (Dop) and \( \text{KNbWO}_6 \cdot \text{H}_2\text{O}:0.125\text{Eu}^{3+} \) (HydDop), calculated with PBEsol functional and \( U \) method.

| Model     | Lattice constants (Å) | Volume (Å³)   |
|-----------|----------------------|---------------|
|           | \( a \)  \( b \)  \( c \) | Calc.  Exp.   |
| Orig      | 10.37  10.41  10.37  | 1120.46  1112.84 [13] |
| Hyd       | 10.50  10.52  10.39  | 1149.32  1160.04 [23] |
| Dop       | 10.38  10.33  10.36  | 1111.51  –         |
| HydDop    | 10.45  10.50  10.39  | 1138.72  1144.44 [13] |

Figure 2 shows the crystalline structures of Hyd, Dop and HydDop models in ball-and-stick view. When hydrating the original \( \text{KNbWO}_6 \) to \( \text{KNbWO}_6 \cdot \text{H}_2\text{O} \), water molecules were found to penetrate into the hollow spaces where the \( K^+ \) cations already reside, resulting in the volume expansion, as shown in Fig. 2(a). One can see that the water molecules are located on the inner side of the hollow spaces and thus the \( K^+ \) cations move to the outer side when compared with the non-hydrated pyrochlore, getting closer to the neighboring oxygen atoms. On the other hand, the \( K^+ \) cations in the Dop model maintain their locations as in the Orig model, while the inserted \( \text{Eu}^{3+} \) ion is clearly away from the BVS tetrahedron, as shown in Fig. 2(b) and (c). In fact, due to its higher valence, \( \text{Eu}^{3+} \) ion tends to interact more strongly with the neighboring \( O^{2−} \) anions than \( K^+ \) cation, so that it resides in the middle position between the hollow spaces. It should be noted that such strengthening of the \( \text{Eu}−\text{O} \) binding leads to the contraction of volume when doping Eu into the defect pyrochlore oxide.

We further consider local symmetry of the \( \text{Eu}^{3+} \) ion in the hosts, which plays a critical role in luminescence as it determines the emission wavelength and intensity due to the intraconfigurational \( 4f−4f \) transition [32,33]. It is well known that for the case of \( \text{Eu}^{3+} \) ion being at an inversion symmetry site, the electric dipole \( ^3\text{D}_0−^3\text{F}_1 \) transition is parity forbidden, while the magnetic dipole \( ^3\text{D}_0−^3\text{F}_1 \) transition is parity allowed with dominant emission wavelength around 590 nm. Meanwhile, at a non-inversion symmetry site, the \( \text{Eu}^{3+} \) ion is known to exhibit electric dipole \( ^3\text{D}_0−^3\text{F}_1 \) transition with emission wavelength of 610 – 620 nm, of which intensity is hypersensitive to the site symmetry of \( \text{Eu}^{3+} \) [31]. In several Eu-doped pyrochlore oxides with luminescence, both the electric and magnetic dipole transitions appear simultaneously, one of which is much stronger in most cases [11,12,32,33]. In the case of defect pyrochlore oxide \( \text{KNbWO}_6 \), the location of doped \( \text{Eu}^{3+} \) could be a highly symmetric site with inversion symmetry for ordering distribution of Nb/W on the B sites (see Fig. S2). For truly random distribution of Nb/W atoms, however, the local symmetry of \( \text{Eu}^{3+} \) is lowered, so that the electric dipole \( ^3\text{D}_0−^3\text{F}_1 \) transition as well as the magnetic dipole \( ^3\text{D}_0−^3\text{F}_1 \) transition can be observed [13]. In addition, the random location of surrounding \( K^+ \) ions inside the hollow spaces, due to their fractional occupancy of 1/4, can also lower the site symmetry of \( \text{Eu}^{3+} \) ion. In this context, one can see that due to existence of water molecules in the hollow spaces, the distribution of \( K^+ \) ions in the HydDop model is more symmetric than in the Dop model. Therefore, the
hysensitive electric dipole $^5D_{2} \rightarrow ^7F_{3}$ transition is more likely in the dehydrated Dop model, in qualitative agreement with the experimental observation [13].

3.2. Electronic structure

Using the optimized models, i.e. Orig, Hyd, Dop and Hyd-Dop models, with the lowest total energies, we calculated their electronic structures by means of PBEsol + $U$ method to investigate the luminescent properties. First, those of the undoped Orig and Hyd models are discussed. In these models, the band structures for spin-up and spin-down states were found to be identical each other, and thus those for spin-up states were only shown in Fig. S3. The band gaps were calculated to be 3.00 eV for the defect pyrochlore oxide KNbWO$_6$ (Orig) and 3.03 eV for the hydrated KNbWO$_6$·H$_2$O (Hyd), which can be said to be in reasonable agreement with the experimental value of 3.50 eV [14] compared with other GGA calculations for semiconductors, indicating the suitability of our selected $U$ values. The almost identical band gap of the hydrated pyrochlore oxide with the original dehydrated one indicates that the water molecules inside the crystal hardly affect the electronic structure of host material. Figure 3 displays the density of states (DOS) for the spin-up states, projected on atomic orbitals. In both the cases of Orig and Hyd models, the valence bands (VBs) were found to be dominantly originated from the O 2$p$ states, while the conduction bands (CBs) to be composed of the 4$d$/5$d$ states of Nb/W atoms and the O 2$p$ states. For the case of Hyd model, the electronic states of O and H atoms of water molecule appeared in VBs, being localized compared with the O 2$p$ states of host. None of states of water molecule are observed in CBs, again indicating the relatively weak interaction between water molecules and host material.

Next, the electronic structure of the Eu-doped defect pyrochlore oxide KNbWO$_6$·0.125Eu$^{3+}$ (Dop model) is shown in Fig. 4. Due to different characteristics, we show the energy band structures and DOS for both the spin-up and spin-down states. As shown in Fig. 4(a), band gap was estimated to be the same to the Orig model as 3.00 eV, and an unoccupied band was found above the valence band maximum (VBM), denoted by dotted line. To clarify which atom contributes to this unoccupied band, the square of band-decomposed wave function at the Γ point of Brillouin zone (BZ) was plotted in Fig. 4(b). The iso-surface of the wave function square was found mostly around Eu atom and partially around nearby O atoms (Fig. 4(c)), indicating that this band is attributed to Eu atom. In the orbital-resolved partial DOS (PDOS) plotted in Fig. 4(d), some of spin-up Eu 4$f$ states can be found at the position of ~ 3 eV below VBM, corresponding to the six occupied 4$f$ orbitals, and one spin-up Eu 4$f$ state is seen above VBM, just being responsible for the unoccupied 4$f$ orbital of Eu$^{3+}$ ion. In the region of conduction band, spin-down 4$f$ states and 5$d$ states of Eu were found above CBM. It should be noted that except Eu states, the other elements of host material have almost the same characteristics to the Orig model: VB mostly comes from O 2$p$ states and CB is composed of the 4$d$/5$d$ states of Nb/W atoms.

Figure 5 displays the electronic structure of the hydrated Eu-doped pyrochlore oxide KNbWO$_6$·H$_2$O·0.125Eu$^{3+}$ (Hyd-Dop model), calculated with the PBEsol + $U$ method. As shown in

![Figure 3: Density of states (DOS) for (a) defect pyrochlore oxide KNbWO$_6$ (Orig model) in the full energy range from -75 eV to 10 eV, where the inset shows DOS around the Fermi level in detail, and (b) hydrated defect pyrochlore oxide KNbWO$_6$·H$_2$O (Hyd model) in the energy range from -7 eV to 6 eV, calculated by using PBEsol + $U$ method.](image)

![Figure 4: Electronic structure of Eu-doped defect pyrochlore oxide KNbWO$_6$·0.125Eu$^{3+}$ (Dop model), calculated with PBEsol + $U$ method. (a) Energy band structure for spin-up and spin-down sates with dotted line for unoccupied band and unchanged band gap of 3.00 eV, (b) isosurface view of wave function square at Γ point, corresponding to unoccupied Eu 4$f$ state and (c) its magnified view indicated by dotted circle in (b), and (d) atomic orbital-resolved partial DOS.](image)

![Figure 5:](image)
host material interact with doped Eu\(^{3+}\) ion as well as the host compound, driving the non-radiative energy transfer between activator Eu\(^{3+}\) ion and the host.

### 3.3. Effect of oxygen vacancy on luminescence

In general, point defects play a critical role in luminescence since they can act as traps for photo-generated electrons, leading to the non-radiative recombination \[^{[20]}\,^{[35]}\]. Considering that the oxygen vacancy V\(_O\) is the dominant point defect with the lowest formation energy in oxides, we investigated only the effect of oxygen vacancy on luminescence. Simulating oxygen vacancies with different charge states V\(_O^\pm\) is not problem for the Orig and Hyd models: removing one oxygen atom and giving the charge \(\pm q\) to the O-removed model. For the cases of Eu-doped models (i.e., Dop and HydDop), however, the conferred charge on the model could be captured by Eu\(^{3+}\) ion (becoming Eu\(^{2+}\) ion) rather than by oxygen vacancy V\(_O\). To verify the charge state of Eu ion in existence of V\(_O\), we calculated the band structures of KNbWO\(_6\):Eu\(^{2+}\) model and Dop+V\(_O\) models with different total charges of \(-1\), \(0\), \(+1\) and \(+2\) (see Fig. S4). It turned out that the band structures of the Dop+V\(_O\) models with total charges of \(-1\), \(0\) and \(+1\) have a characteristic feature of KNbWO\(_6\):Eu\(^{2+}\) – extremely localized flat bands from the seven Eu 4\(f\) spin-up states in the middle of band gap region – whereas the Dop+V\(_O^2\) model resembles that of KNbWO\(_6\):Eu\(^{3+}\). Therefore, the Dop+V\(_O\) models with total charges of \(-1\), \(0\), \(+1\) and \(+2\) represent the defect states of Eu\(^{2+}\)/V\(_O^\pm\), Eu\(^{3+}\)/V\(_O^\pm\), Eu\(^{2+}\)/V\(_O^2\) and Eu\(^{3+}\)/V\(_O^2\), respectively.

We estimated the formation energies of these oxygen vacancies using the following equation \[^{[35]}\]:

\[
E_f(V_O^\pm) = E(\text{perf} + V_O^\pm) - E(\text{perf}) + \mu_O + q\varepsilon_F + E_{\text{MP}}
\]  

where \(E(\text{perf} + V_O^\pm)\) and \(E(\text{perf})\) are the total energies of compounds with and without \(V_O^\pm\), \(\mu_O\) the chemical potential of oxygen, \(\varepsilon_F\) the Fermi energy and \(E_{\text{MP}}\) the Makov-Payne correction term for the finite size effect of charged model. Here, \(\mu_O\) was estimated to be half the total energy of isolated oxygen molecule, and \(\varepsilon_F\) could be defined referencing to the VBM of the host as \(\varepsilon_F = \varepsilon_{\text{BM}} + \Delta \varepsilon_F\), where \(\Delta \varepsilon_F\) is varying between 0 and band gap \(E_g\) \[^{[46]}\,^{[37]}\]. Table 3 lists the calculated formation energies \(E_f(V_O^\pm)\) by using VBM as \(\varepsilon_F\). It was revealed that in each case of different models, V\(_O^2\) had the lowest formation energy, indicating that it is the oxygen vacancy with the highest possibility in the KNbWO\(_6\)-derived compounds, regardless of being hydrated or Eu doped. The Eu\(^{2+}\) doping was found to make it easy for oxygen vacancy to be generated due to lowering the formation energy when Eu\(^{2+}\) doping in most cases, by comparing between Orig and Dop or Hyd and HydDop. It should be highlighted that when compared with Eu\(^{2+}\)/V\(_O^\pm\), Eu\(^{3+}\)/V\(_O^\pm\) has remarkably higher formation energy, indicating that with oxygen vacancy the charge state of Eu\(^{3+}\) is readily reduced to Eu\(^{2+}\) with a half-filled electron configuration. Above discussion shows that O vacancies in this compound may act as a donor to reduce Eu\(^{3+}\) to Eu\(^{2+}\). In fact, similar mechanism by Ba vacancy defect (V\(_{\text{Ba}}\)) acting as a donor, was proposed to explain the reduction of Eu\(^{3+}\) to Eu\(^{2+}\) observed in BaAl\(_2\)O\(_3\):Eu phosphor prepared.

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Fig. 5(a) for its energy band structure, the band gap was calculated to be 2.73 eV, being 0.30 eV lower than the value (3.03 eV) of the undoped Hyd model, due to an up-shift of VBM attributed to two spin-down bands. Like in the Dop model, one unoccupied spin-up band was found over VBM, corresponding to the unoccupied Eu 4\(f\) state, as shown in Fig. 5(b) for the isosurface of band-decomposed wave function square at the \(\Gamma\) point. Meanwhile, the two occupied spin-down bands were revealed to be originated from oxygen atoms of water molecules, as demonstrated in Fig. 5(c). It is worth noting that such uplift of spin-down bands is not observed in the Hyd model, indicating that this is caused by interaction between the doped Eu\(^{3+}\) ions and the water molecules. Such interaction effect is more noticeable in atomic orbital-resolved PDOS analysis shown in Fig. 5(d). When compared with the dehydrated Eu-doped Dop model (Fig. 5(a)), the spin-up Eu 4\(f\) states are found to be also divided into the occupied and unoccupied parts, but the unoccupied state is observed to be clearly up-shifted from the valence band of host material. In addition, the location of spin-down Eu 4\(f\) states relative to spin-up ones is more or less the same to Dop model, but all the Eu 5\(d\) states move higher on energy scale. When compared with the hydrated Hyd model (Fig. 5(b)), the occupied O 2\(p\) states of water molecule are clearly shown to be up-lifted over the valence band of host material. To sum up, it can be concluded that the water molecules in the hydrated...
under thermal carbon-reducing condition. Once the Eu$^{3+}$ is reduced to Eu$^{2+}$, it would exhibit characteristic broad emission spectra at around 500 nm due to $4f-5d$ transition, in contrast to sharp peaks in emission spectra of Eu$^{3+}$. However, in our previous experiment, the absorption and emission spectra were found to be originated from the intra- configurational $4f-4f$ transitions of Eu$^{3+}$, and no characteristics of $4f-5d$ transitions of Eu$^{2+}$ was found. Thus, once the doped Eu$^{3+}$ ion is reduced to Eu$^{2+}$, it can no longer act as luminescence centre in this material, indicating that the oxygen vacancies are detrimental to luminescence. It is worth noting that all the $E_f(V_0^q)$ values in the hydrated compounds are higher than in case of dehydrated ones, indicating that water molecules inside the host structural framework suppress the formation of oxygen vacancies.

For the charged oxygen vacancies, their formation energies may change from $V_0^q$ to $V_0^{q+}$ (or vice versa) by trapping or releasing the activated electron, and this energy level is defined as charge state transition energy $E_f(V_0^q)$. In the bottom part of Table 3, the transition energies estimated by inspecting Fig. 6 were listed. It was clearly revealed that the transition energies in the Eu-doped models were found in the higher Fermi energy close to the CBM, whereas they were located in the middle of band gap region. Importantly, $E_f(V_0^{q+})$ were estimated to be 2.68 and 2.63 eV in the Dop and Hyddop models, which are close to the transition energy 2.67 eV of Fe$^{3+}$ to Fe$^{2+}$ being responsible for major peak of 464 nm in absorption spectra [13]. This indicates that the oxygen vacancy in the Dop and Hyddop models can act as a trap for electrons excited by incident radiation of 464 nm.

3.4. Ln$^{3+}$ doping into KNbWO$_6$ (Ln = Ce, Pr, Nd, Pm, Sm)

Finally, we investigated the crystalline and electronic structures of other trivalent Ln ion doped pyrochlore oxides KNbWO$_6$.0.125Ln$^{3+}$ (Ln = Ce, Pr, Nd, Pm, Sm) with a calculation of doping energy. As mentioned above, when the Ln$^{3+}$ ion is doped into the pyrochlore oxide host KNbWO$_6$, three K$^+$ cations should be removed from the host to satisfy the charge neutrality. Then, the doping process can be thought to occur through (1) taking away three K atoms from the Orig model, leading to formation of intermediate phase, and (2) inserting one Ln atom into the intermediate phase to reach the Ln-doped compounds. For instance, the binding energies between the intermediate phase and three K atoms and one Eu atom can be calculated as follows,

\[E_d(3K) = E(int) + 3E(K) - E(Orig)\]  
\[E_d(Eu) = E(int) + E(Eu) - E(Dop)\]

where $E(int)$, $E(Orig)$ and $E(Dop)$ are the total energies of the crystalline compounds in the intermediate phase, Orig and Dop model, and $E(K)$ and $E(Eu)$ are the total energies of isolated K and Eu atoms, respectively. Then the doping energy can be calculated as follows,

\[E_{dop} = E(Dop) - E(Eu) + 3E(K) - E(Orig) = E_d(3K) - E_d(Eu)\]

Likewise, the doping energy in case of the hydrated compound can be estimated from total energies of Hyd model $E(Hyd)$ and Hyddop model $E(Hyddop)$.

Table 4 presents the optimized lattice constants and unit cell volumes of the Ln-doped pyrochlore oxides KNbWO$_6$.0.125Ln$^{3+}$ (Ln = Ce, Pr, Nd, Pm, Sm, Eu) and their doping energies. As increasing the atomic number of Ln dopant ion, the lattice constants and thus the unit cell volume were found to gradually decrease; for the unit cell volume from 1115.82 Å$^3$ for Ce- to 1111.04 Å$^3$ for Eu-doped compounds.
Table 4: Lattice constants \((a, b, c)\), unit cell volume and doping energy of 
\(\text{K NbWO}_6:0.125\text{Ln}^{3+}\) \((\text{Ln} = \text{Ce, Pr, Nd, Pm, Sm, Eu})\), calculated by using 
PBEsol + \(U\) method.

| Dopant | Lattice constants \((A)\) | Volume \((\text{Å}^3)\) | \(E_{\text{dop}}\) (eV) |
|--------|--------------------------|-----------------|-----------------|
| Ce     | 10.39 10.34 10.38        | 1113.82         | 0.10            |
| Pr     | 10.39 10.34 10.38        | 1114.60         | 0.13            |
| Nd     | 10.39 10.33 10.37        | 1113.72         | 0.19            |
| Pm     | 10.39 10.33 10.37        | 1112.83         | 0.28            |
| Sm     | 10.38 10.33 10.37        | 1112.04         | 0.39            |
| Eu     | 10.38 10.33 10.36        | 1111.31         | 0.48            |

Figure 7: Partial density of states in 
\(\text{Ln-doped pyrochlore oxides} \text{K NbWO}_6:0.125\text{Ln}^{3+}\) \((\text{Ln} = \text{Ce, Pr, Nd, Pm, Sm, Eu})\), calculated by using 
PBEsol + \(U\) method.

Such gradual decrease in the unit cell volume can be attributed to decrease of the ionic radius of \(\text{Ln}^{3+}\) ion as increasing the 
atomic number. The doping energy was also found to system-
atically change; it increases from 0.10 eV for Ce-doping 
to 0.48 eV for Eu-doping. This indicates that doping Ln into 
\(\text{K NbWO}_6\) is getting more difficult going from Ce to Eu. Con-
versely, \(\text{K NbWO}_6\) can be said to serve as a better host material 
for \(\text{Ce}^{3+}\) doping than for \(\text{Eu}^{3+}\). For the case of Eu-doping into the 
Hyd model, the doping energy was calculated to be 0.57 eV, 
which is higher than into the Orig model (0.48 eV), indicating 
that the doping is more favorable in the dehydrated compound.

Figure 7 shows the atomic orbital-resolved PDOS in the 
\(\text{Ln-doped pyrochlore oxides}, \text{highlighting the PDOS of Ln 5d and}
\text{4f states in the grey background of total DOS. In all the \(\text{Ln-doped}
\text{compounds, the band gap identified by TDOS was found to barely}
\text{change for different Ln ions but to be fixed at ~3 eV. Commonly, the \(\text{Ln}^{3+}\)
\text{ions contain seven 4f orbitals, which are divided into occupied and unoccupied states. The number of \text{occupied states corresponding to the spin-up electrons increases from 1 for Ce\(^{3+}\) to 6 for Eu\(^{3+}\), while the unoccupied orbitals are for mostly spin-down states and some spin-up states. In the case of Ce\(^{3+}\)-doped compound, the occupied spin-up state was found over the VBM, but in other cases they were located below the VBM. On the other hand, the unoccupied states were found above the CBM in the cases of Ce\(^{3+}\) and Pr\(^{3+}\)-doped compounds, whereas they were found to gradually move towards the VBM going from Nd\(^{3+}\) through Pm\(^{3+}\) to Sm\(^{3+}\). Even, the unoccupied spin-up 4f state of Eu is located just above the VBM, as discussed above. It should be noted that as increasing the atomic number of Ln ion, all the spin-up 4f states move downward, while the unoccupied spin-down 4f states move upward. Such tendency of 4f state positioning was observed by first-principles study on the series of \(\text{Ln}^{3+}\)-doped \(\text{LaSi}_2\text{O}_5\) \((\text{Ln} = \text{Ce, Pr, Nd, Pm, Sm, Eu})\) luminescent materials \([39]\). These imply that the defect pyrochlore oxides \(\text{K NbWO}_6\) doped with \(\text{Ln}^{3+}\) can also exhibit luminescent property, and therefore, further 
experimental studies are required to verify their potentiali-
ties as luminescent materials.

4. Conclusions

In this study, we have carried out the first-principles calcu-
lations to clarify the several factors affecting luminescence 
properties of defect pyrochlore oxide \(\text{K NbWO}_6\)-based 
materials. Several unit cell models have been suggested for 
crystalline \(\text{K NbWO}_6\), its hydrated phase \(\text{K NbWO}_6\cdot\text{H}_2\text{O}\), Eu-
doped phase \(\text{K NbWO}_6\cdot0.125\text{Eu}^{3+}\) and hydrated Eu-doped 
phase \(\text{K NbWO}_6\cdot\text{H}_2\text{O}\cdot0.125\text{Eu}^{3+}\), in consideration of random 
distribution of Nb/W atoms, water molecule and Eu positions. Structural optimizations revealed that the local symmetry of \(\text{Eu}^{3+}\) ion can be lowered in the dehydrated phase, giving the expla-
nation for the experimental result of 10 times weaker emis-
sion at 612 nm owing to electric-dipole \(\text{5D}_0\rightarrow\text{7F}_2\) by anneal-
ing. Through the electronic structure calculations, the band 
gap of the host has been found to be almost the same as ~3 
eV in all the \(\text{K NbWO}_6\)-derived compounds. From the calcu-
lated DOS of \(\text{K NbWO}_6\), the occupied spin-up 4f 
states of \(\text{Eu}^{3+}\) ion were found below the VBM of the host, 
while the unoccupied spin-up state was found above the VBM. The observed up-shift of the unoccupied spin-up state from 
the VBM in \(\text{K NbWO}_6\cdot\text{H}_2\text{O}\cdot0.125\text{Eu}^{3+}\) indicates that water
molecules could interact with host and Eu$^{3+}$ ion, mediating the non-radiative energy transfer between them and causing the quenching effect. When introducing the oxygen vacancy, Eu$^{3+}$ ion was found to be readily reduced to Eu$^{2+}$, leading to detriment to luminescence property, and moreover $V_0$ was found to act as traps for the electrons activated by incident light of 464 nm. Finally the crystalline and electronic structures of KNbWO$_6$ doped with other Ln ions (Ln = Ce, Pr, Nd, Pm, Sm) have been investigated, concluding that KNbWO$_6$ can also be used as luminescent host for doping a series of Ln$^{3+}$ ions.

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