BAND EDGE SINGULARITIES AND DENSITY OF STATES IN $YTaO_4$ AND $YNbO_4$

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Abstract

We study the structural and electronic properties of $YTaO_4$ and $YNbO_4$ by means of accurate first-principle total energy calculations. The calculations are based on density functional theory (DFT). The total energy, electronic band structure, and density of states are calculated via the full potential linear-augmented plane wave approach, as implemented in the WIEN2K code, within the framework of DFT. The results show that the valence bands of tantalate and niobate systems are from O *2p* states. Conduction bands are divided into two parts. The lower conduction band is mainly composed of Ta *5d* or Nb *4d* states and the upper conduction bands involve contribution mainly from Y *4d* states of $YTaO_4$ or $YNbO_4$. The efficient band gaps in yttrium tantalate and niobate are determined about 4.8 and 4.1 eV, respectively. The agreement between the calculations and the experimental data is excellent. The efficient band gap and a simple model illustrating excitation and emission process in considered host lattices are discussed.
Keywords: Electronic properties; $YTaO_4$; $YNbO_4$; Luminescence

1. Introduction

A short while ago we reported the first evidence of the luminescence and structural properties of double activated $Y(Ta,Nb)O_4:Eu^{3+}Tb^{3+}$ phosphors [1]. These data allowed us to calculate the crystal structure of M'-$YTaO_4$ and M-$YNbO_4$ host lattices. As it is well-known, performances of these phosphors and luminescence properties strongly depend on their crystal structure. However, some fundamental questions concerning host lattice emission and charge transfer transitions still remain unanswered.

In the last decade, some efficient methods based on density functional theory (DFT) were applied to niobate system doped with Bi [2-4]. To the best of our knowledge, no work has been reported using first-principles calculations based on the DFT to give a reasonable interpretation to host lattice. Even though tantalate and niobate phosphors are well-known, there have been no theoretical approaches to interpret their luminescence. In this paper electronic band structure and density of states (DOS) are calculated via the full potential linear-augmented plane wave approach, as implemented in the WIEN2k code [5], within the framework of DFT. WIEN2k is based on the method which is among the most precise and reliable ways to calculate the electronic structure of solids. We believe that this approach provides a suitable first-principles framework for making direct comparisons with experimental spectra. The calculating scheme is described in detail elsewhere and so we provide only the bare essentials here. Thus, the nature of

optical excitations near the band gap of $YTaO_4$ and $YNbO_4$ was clarified using the first-principles calculations. The efficient band gap corresponding to real data and simple model illustrating the emission process in tantalate and niobate systems are discussed.

2. Samples preparation and experimental procedure

Several series of yttrium tantalate and niobate phosphors were prepared by solid state reaction method from a homogeneous mixture consisting of Y_2O_3 (99.9%) and Nb_2O_5 or Ta_2O_5 (Optipur) [1]. Na_2SO_4 was used as flux. The mixtures were homogenized with a ball mill, in acetone medium, and dried at 70°C. The phosphor samples were baked at 1200°C for 4 h and slowly cooled to room temperature. Finally, the samples were water washed, dried, and then sieved.

The samples were investigated using X-ray diffraction (Rigaku X-ray Diffractometer), UV and VUV excitation luminescence, and first-principles quantum-mechanical calculations were applied in order to study their structural and luminescent properties. UV measurements were monitored using a Perkin-Elmer LS50B spectrometer with a xenon flash lamp. VUV excitation spectra of samples were measured using a VUV spectrophotometer equipped with a VUV monochromator (ARC, VM 502) and a light source of a 30-W deuterium lamp (ARC, DS775-100).

3. Results and discussion

Figure 1 shows the excitation spectra from $YTaO_4$ (1) and $YNbO_4$ (2). The photoluminescence excitation (PLE) spectra were measured in a VUV range of 100 to 350 nm using sodium salicylate powder as a reference. The excitation spectra were obtained by observing all emission light and calibrated by that of sodium salicylate, which has constant quantum efficiency in the 115–350 nm range. Three obvious large bands A, B, and C in the VUV PLE spectra are seen for both host lattices, but more clearly they are seen for $YTaO_4$ (1).

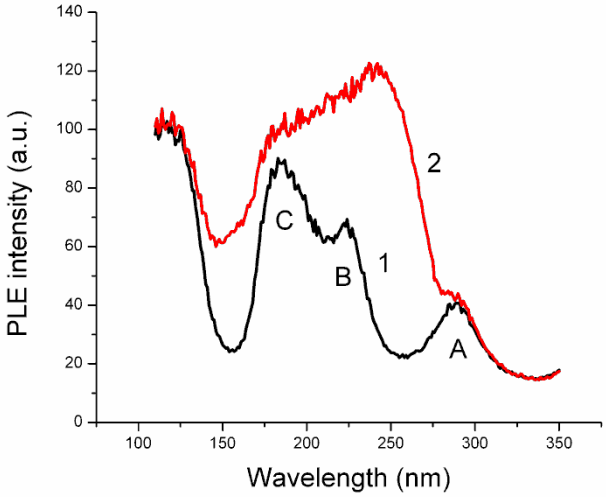

Fig. 1. PLE spectra for $YTaO_4$ (1) and $YNbO_4$ (2) under VUV excitation.

The nature of the band A is not yet determined up today and we made here an assumption to clarify it. We believe that the other two bands observed in the VUV range in tantalate and niobate systems are related to the following processes.

We associate the band B around 220 nm with the absorption of the host lattices. The TaO_4^{3-} and NbO_4^{3-} groups can absorb excitation energy through $O^{2-} \rightarrow Ta^{5+}$ and $O^{2-} \rightarrow Nb^{5+}$ host charge transfer transition, respectively. These bands are shifted in tantalate and niobate systems due to different structure groups.

The band C peaked around 170 nm is probably related to the host absorption. The Y-O bonds are excited and the energy is transferred to host lattice. The position of this band C for Y^{3+} ions can be calculated with the help of an empirical formula given by Jorgensen [6]:

$$E_{CT} = [(X)-(M)] \times 30.000 \text{ cm}^{-1}.$$

Here E_{CT} gives the position of the charge transfer band (CTB) in cm^{-1}, (X) the optical electronegativity of the anion, and (M) that of the central metal ion. Using Pauling scale for electronegativity [7], namely, (O)=3.44 and (Y)=1.22, the CTB of Y-O can be estimated near 67.000 cm^{-1}, or around 150-160 nm. The position of the band C is the same for $YTaO_4$ and $YNbO_4$ because it is determined only by electronegativity Y and O and does not depend on tantalate or niobate groups.

To check this assumption and to explain the nature of the band A, we compared PLE spectra with DOS calculations separately for $YTaO_4$ (Fig. 2) and $YNbO_4$ (Fig. 3).

The crystalline structures of phosphors were determined by XRD measurements on the basis of Synchrotron X-ray Diffraction patterns (Pohang Accelerator Laboratory, Korea) and the atomic positions of all the elements are presented in Table 1.

We calculated the electronic structure of host lattices $YTaO_4$ and $YNbO_4$ in terms of DFT. In the initial approximation, the exchange correlation energy of electrons was described in the generalized gradient approximation (GGA) within the scheme of Perdew et al. GGA96 [8] to determine the total energy, band structure, and DOS.

Table 1. Atomic positions and lattice parameters in $YTaO_4$ and $YNbO_4$

M'-$YTaO_4$	*Atom*	*x*	*y*	*z*	*F*
a=5.29568Å	Y	0.25	0.76523	0	1
b=5.445447Å	Ta	0.25	0.30632	0.5	1
c=5.10940Å	O(1)	0.49619	0.43402	0.27800	1
β=96.39119	O(2)	0.09912	0.09079	0.24181	1
M-$YNbO_4$	*Atom*	*x*	*y*	*z*	*F*
a=7.61851Å	Y	0	0.37891	0.25	1
b=10.94611Å	Nb	0	0.85620	0.25	1
c=5.29745Å	O(1)	0.20166	0.78039	0.20515	1
β=138.43617	O(2)	0.25050	0.96246	0.65526	1

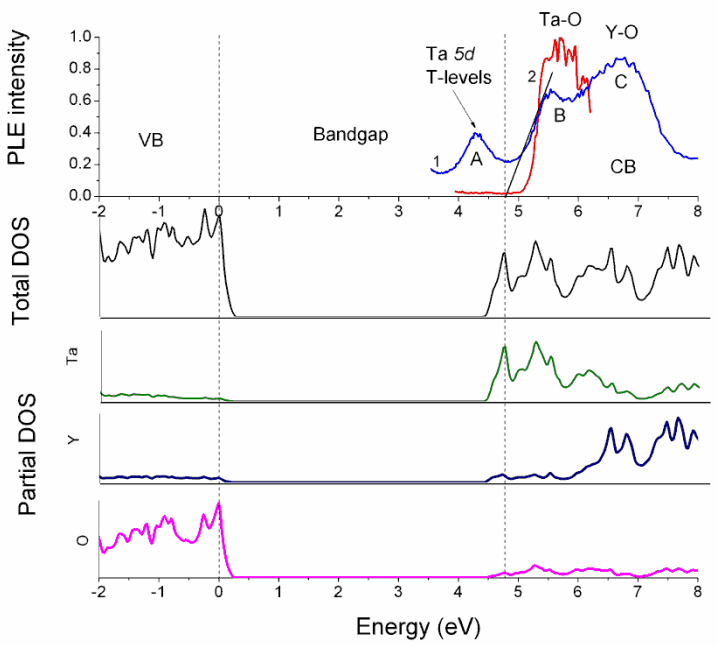

Fig. 2. $YTaO_4$; PLE spectra under VUV (*1*) and UV (*2*) excitation (λ_{em} = 330 nm). Below is the Total density of states of $YTaO_4$ and Partial density of states of Ta, Y and O.

In Fig. 2, the total DOS, as well as partial DOS, is combined together with PLE under VUV (1) and UV (2) excitations taken in the electron volts as DOS. This comparison helps us to identify and explain the nature of excitation bands and to determine correctly the band gap in $YTaO_4$ and $YNbO_4$.

Worthy of note that the GGA sometimes gives quantitatively incorrect results for solids which contain strongly localized electrons such as transition-metals and rare-earth oxides. However according to our GGA calculations we can propose the following assumption.

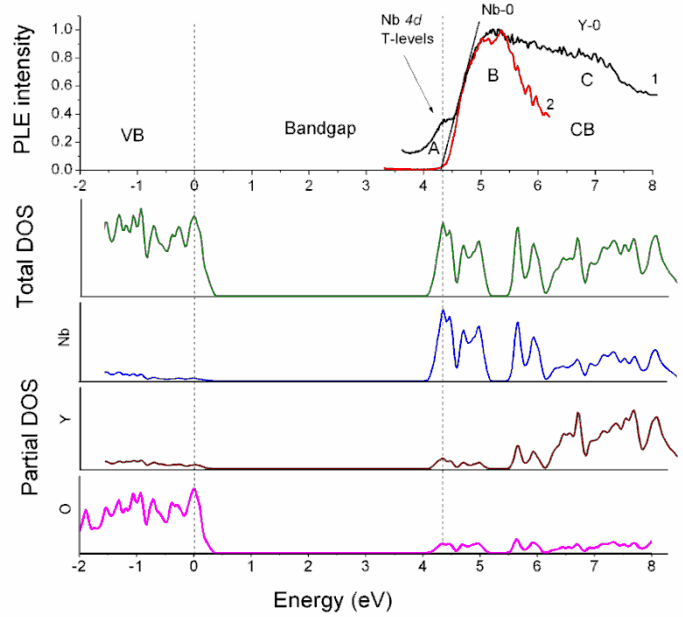

Fig. 3. $YNbO_4$; PLE spectra under VUV (*1*) and UV (*2*) excitation (λ_{em} = 400 nm). Below is the Total density of states of $YNbO_4$ and Partial density of states of Nb, Y and O.

Only main *p*-like state for oxygen and *d*-like states for yttrium, tantalum, and niobium are presented in Figs. 2 and 3. The valence band (VB) of $YTaO_4$ (left side in Fig. 2) and $YNbO_4$ (Fig. 3) mostly consists of O *2p* states. Conduction band (CB) (right side in Figs. 2 and 3) is divided into two parts. The lower conduction band (4 to 6 eV) is mainly composed of Ta *5d* or Nb *4d* states and the upper conduction band (6-8 eV) involves contribution mainly from Y *4d* states. The charge transfer gap between Ta and O (Fig. 2) and Nb and O (Fig. 3) is clearly shown and it is different for tantalate and niobate phosphors.

In both Figs. 2 and 3 VUV (*1*) and UV (*2*) fragments of excitation spectra of the host lattices are presented and combined with total and partial density of states. To make partial DOS more visible, we have enhanced its magnitude. Tantalum and yttrium (Fig. 2) as well as niobium and yttrium distribution (Fig. 3) in partial DOS explain completely the nature of the bands B and C in excitation spectra. The band C in the VUV PLE spectra is associated with the absorption of the host lattice, which involves mostly the transitions between *4d*-like states of Y and *2p*-like states of O or Y^{3+}-O^{2-} charge transfer transition. The band B is a hybrid band in both materials and it is composed of both [Y-O] and [Ta-O] or [Y-O] and [Nb-O] charge transfer transitions. In UV excitation spectrum (*2*), all the resolved lines correspond to partial DOS of Y and Ta or Nb peaks.

If the high energies X-ray, electron beam or VUV excitations are applied, it would be quite reasonable to assume that the excitation energy is absorbed first by the host lattice, which involves the transition between *4d*-like states of Y and *2p*-like states of O. The absorbed energy may then be transferred to TaO_4 or NbO_4 groups and last transferred to the activator center if any. This process is shown in Fig. 4.

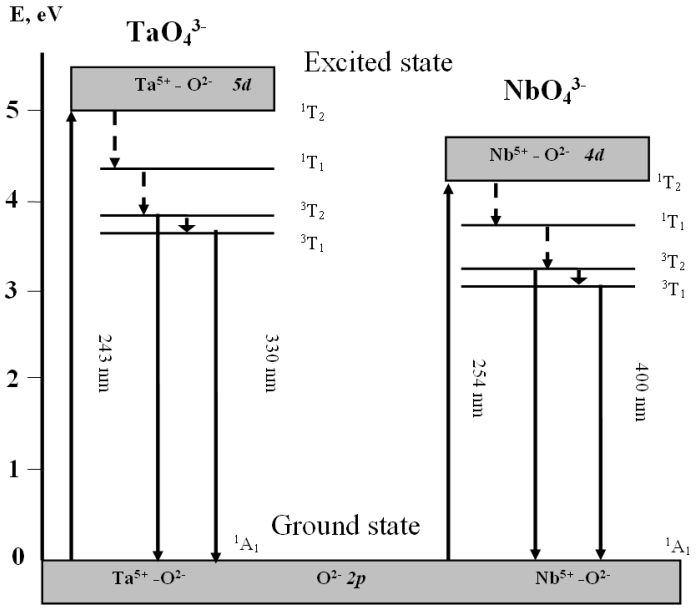

Fig. 4. Simple model illustrating the excitation and emission processes in $YTaO_4$ and $YNbO_4$.

Figure 4 depicts a simple model illustrating the excitation and emission processes in $YTaO_4$ and $YNbO_4$. For both phosphors, the model is very similar and differs only by the excitation energy and band gap.

For $YTaO_4$ sample, under a 243-nm excitation, a charge-transfer transition from the O^{2-} ion to the Ta^{5+} metal ion occurs. To excite the $YNbO_4$ sample, we use a 254-nm excitation. The

possible excited states of Ta^{5+} and Nb^{5+} are $^3T_1$ (metal to ligand charge-transfer state), $^3T_2$, $^1T_1$, and $^1T_2$ (charge-transfer state), and the ground state is $^1A_1$ [9]. According to a simplified calculation by Ballhausen [10], the order of these levels is $^1T_2 > {}^1T_1 > {}^3T_1 > {}^3T_2$. Only the transition $^1A_1 \rightarrow {}^1T_2$ is allowed as an electric—dipole transition [11]. The absorption edge and the excitation band of the niobates and tantalates correspond to this transition. After excitation, the transitions from the $^3T_2$, $^3T_1$ excited levels to the ground state $^1A_1$ occur and give the broad UV peaked at 330 nm for $YTaO_4$ or blue emission band around 400 nm for $YNbO_4$.

We assume that the position of the level $^1A_1$ corresponds to the zero of O *2p*-like states in total DOS. This level can be considered as zero of valance zone. Position of level $^1T_2$ corresponds to the absorbance edge of about 5 eV for $YTaO_4$ (Fig.2) and 4.1 eV for $YNbO_4$ in Fig. 3. Some lower levels $^1T_1$,$^3T_1$,$^3T_2$ marked as T-levels in Figs .2 and 3 are located in band gap. These T-levels are responsible for the band A in $YTaO_4$ and $YNbO_4$. In addition to the electric-dipole transition, $^1T_1$-$^1A_1$, $^3T_1$ -$^1A_1$ and $^3T_2$ -$^1A_1$ also have a certain nonvanishing transition probability. The singlet-triplet transition can acquire intensity from the allowed transition by spin-orbit coupling. This will be more important for tantalate than for niobate, since the magnitude of the spin—orbit coupling is greater for Ta than for Nb. The $^3T_1$-$^1A_1$ and $^3T_2$-$^1A_1$ transitions will have the higher transition probability for the stronger spin-orbit coupling interaction. The $^1T_1$-$^1A_1$ transition will become more intense for the larger deviation from a cubic symmetry. In view of this point, we can assign the first strong absorption band in order of increasing energy to $^1A_1 \rightarrow {}^3T_1$, $^3T_2$, $^1T_1$ transitions, as shown in Fig. 4. The first level in excited state possible from quantum mechanics $^1T_2$ must be higher than the lowest $^3T_1$, and next $^3T_2$ and $^1T_1$. In this case, the minimal energy of excitation or effective band gap between the first two maxima in VB and CB is 4.8 eV from DOS for $YTaO_4$ (or 4.8-5.1 eV from excitation spectra) and 4.1 eV for $YNbO_4$. These data are in good agreement with experimental results. As noted above, the GGA is not accurate enough for a proper description of strongly correlated systems. In particular the band gap may appear too small in our calculations.

Since the GGA+U method is well established for strongly correlated materials with well localized orbitals its further application to the luminescence structural properties of phosphors is possible. Main idea of GGA+U method consists in separation of electrons into two subsystems: localized d or f electrons for which the Coulomb d-d interaction should be taken into account by a term U in a model Hamiltonian and delocalized s and p electrons which could be described by using an orbital-independent one-electron potential (GGA) [12,13].

It is quite possible that the application of GGA + U method will expand the band gap and give us another interpretation of experimental data.

4. Conclusions

The nature of optical excitations near the band gap of $YTaO_4$ and $YNbO_4$ was clarified using the first-principles calculations. It was shown that the absorption near the band edges involves excitations from the oxygen *2p*-like states near the top of the valence band to the cations of Ta *5d* or Nb *4d* -like states near the bottom of the conduction band.

The proposed model is in good agreement with the experimental results and can be adopted for a better understanding of the transfer mechanism in the host lattices of tantalate and niobate phosphors as well as for improving their optical properties.

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