# Luminescence Behavior of $YNbO_4$ and $YNbO_4$:Bi

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## Abstract

The luminescence behaviors of Yttrium niobate and Bi doped Yttrium niobate were investigated under UV and low voltage electron excitations and interpreted with the first-principle calculations. In the UV excitation and emission spectra of $YNbO_4$ and $YNbO_4$:Bi, we were able to separate host contribution and Bi contribution and found that the shift in emission peak to longer wavelength is mainly due to Bi contribution. Using density functional theory, the cluster calculations were carried out for both $YNbO_4$ and $YNbO_4$:Bi. From the calculated density of states, we were also able to explain the charge transfer gap in the host and the effect of Bi in the excitation and emission spectra theoretically.

## Introduction

$YNbO_4$ itself is known as a blue emission phosphor and the bismuth doped $YNbO_4$ also shows blue emission in the longer wavelength than $YNbO_4$[1]. The recent studies by our group[2] and Vecht et al.[3] showed that the $YNbO_4$:Bi could be used as a low voltage saturated blue phosphor for Field Emission Display(FED).

In this report, we focused the effect of Bi in the blue emission by comparing the cathode- and photo-luminescence of $YNbO_4$ and $YNbO_4$:Bi, both experimentally and theoretically. We have determined optimum conditions of cathodoluminescence (CL) by controlling $Bi^{3+}$ concentration and Y/Nb ratio. The photo-luminescence (PL) emission spectra were obtained for the sample in optimum condition. We have also initiated the calculations on the electronic structure of $YNbO_4$ and $YNbO_4$:Bi using density functional cluster method. The photoluminescence of $YNbO_4$ and $YNbO_4$:Bi will be discussed with the calculated results regarding the charge transfer gap of $YNbO_4$ and the effect of Bi in $YNbO_4$:Bi.

## Experimental

$YNbO_4$ and bismuth doped $YNbO_4$ phosphors have been prepared by solid state reaction technique. The cathodoluminescent (CL) properties were studied by excitation with electrons with energies of 800 eV, 2.4 mA. The optimum conditions to give the maximum CL emission intensity were determined by varying the concentration of $Bi^{3+}$ and Y/Nb ratio. The PL spectra were obtained by single shot measurement with a Perkin Elmer LS 50 luminescence spectrometer with 220 and 310 nm excitations.

## Calculations

We have calculated the electronic structure of $YNbO_4$ and Bi-doped $YNbO_4$ in the framework of density functional theory. The cluster method was employed using $DMol^3$ program[4]. The cluster is embedded in point charge distribution to represent the crystal.

First, we have carried out the cluster calculations for the host material, $YNbO_4$. The Nb-centered 35-atom cluster was taken and embedded in a 304 point charge environment to represent $YNbO_4$ crystal. The atomic positions of the cluster and the point charge distribution are taken from the structural parameters in Ref.[5]. The calculated PDOS (partial densities of states) of the central Nb and the nearest neighboring O are shown in Fig.1-(a). The charge transfer gap between Nb and O is clearly shown. The PDOS of Y is away from the region where we are interested, thus we do not give attention to them in the present report. The details of the this calculation will be published elsewhere [6].

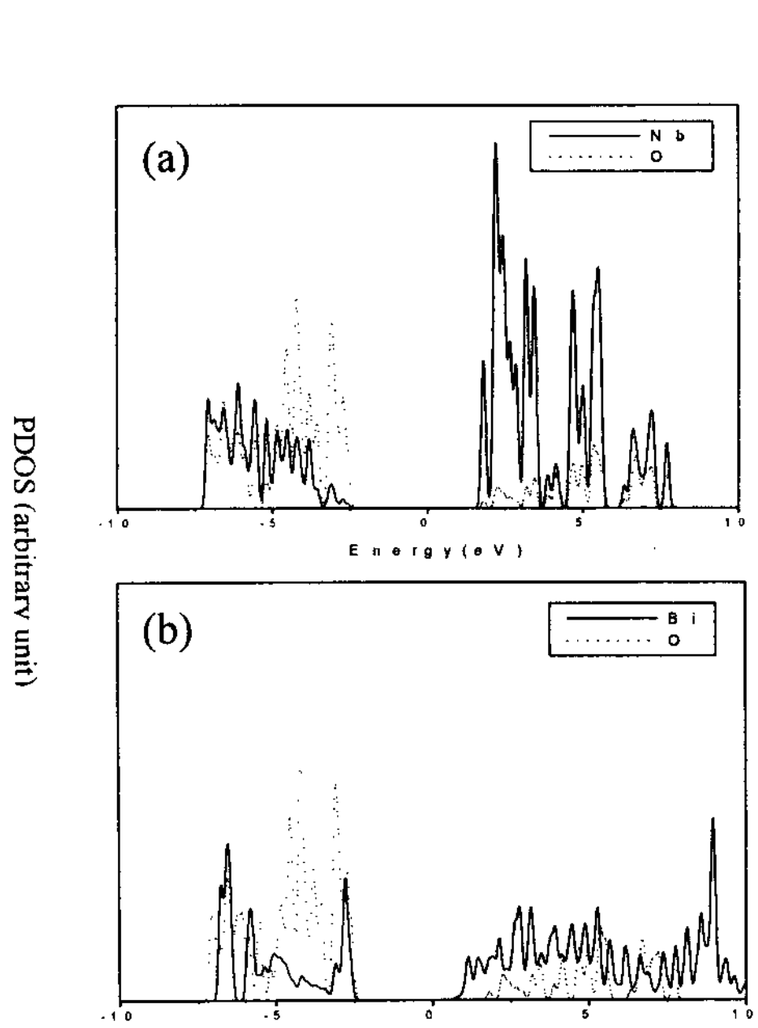


Figure 1. (a)Partial density of states (PDOS) of $YNbO_4$
(b)Partial density of states (PDOS) of $YNbO_4$:Bi

$YNbO_4$:Bi is a well-known blue phosphor. Since Bi is doped in $YNbO_4$ by about 0.2 wt%, we can treat Bi as a point defect in the calculations. A similar cluster method was applied for $YNbO_4$:Bi to investigate the effect of introducing Bi at Y site. When Bi substitutes Y, geometrical relaxation around Bi is expected. Therefore, we had performed geometry optimization using FastStructure [7]. Then we started the cluster calculations with $DMol^3$ from the optimized geometry. A Bi-centered 33 atom cluster was taken and embedded in 241 point charges. The calculated PDOS of Bi and O is shown in Fig. 1-(b). The highest occupied state consists of mainly Bi 6s and O 2p, whereas the lowest unoccupied state consists of Bi 6p. Since Bi is a point defect, we can assume that the charge transfer gap between Nb and O of Bi-doped $YNbO_4$ is not much different from that of undoped $YNbO_4$. From Fig. 1-(a) and (b), one can find that the band gap of the Bi-centered cluster is smaller than that of the Nb-centered cluster. The PDOS of Bi 6p locates in lower energy than those of Nb 4d.

## Results and Discussion

From the CL emission spectrum data, the optimum concentration of $Bi_2O_3$ and Y/Nb ratio were found to be 0.2 wt% and 52/48, respectively. One of the emission spectra is shown in

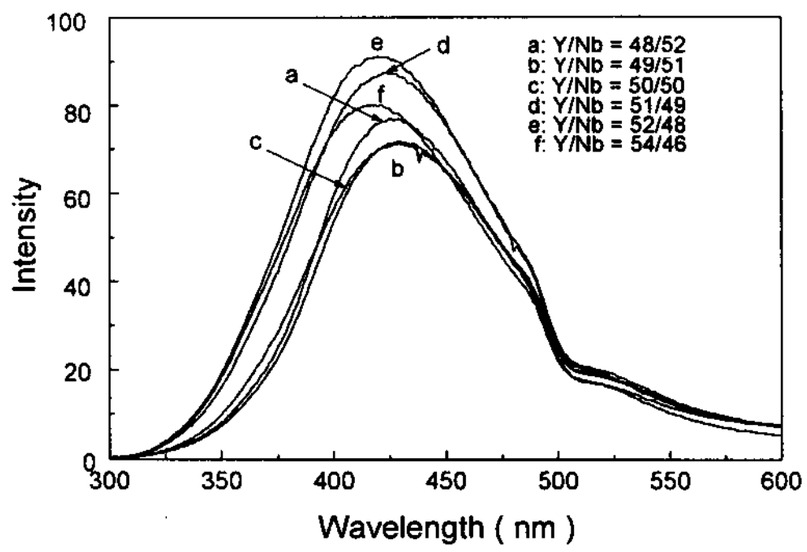


Figure 2. CL emission spectra of 0.2 wt% Bi doped $YNbO_4$ as a function of the Y/Nb ratio(1250℃/4 hrs).

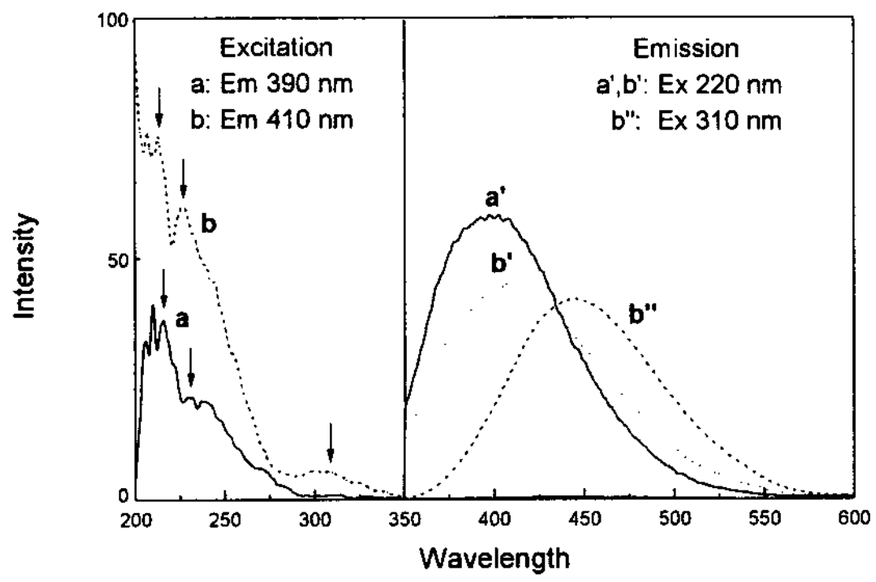


Figure 3. PL excitation and emission spectra of $YNbO_4$(full line) and 0.2 wt% Bi doped $YNbO_4$(dashed or dotted line).

Fig. 2.

The PL excitation and emission spectra of undoped and Bi doped yttrium niobates are illustrated in Fig. 3. The excitation band peaks around 220 and 230 nm are shown for both samples, therefore these bands seem due to the direct excitation of the $YNbO_4$ host itself, via the charge transfer (CT) transition between Nb and O.

For the Bi activated $YNbO_4$ phosphor, a weak third excitation band peaking around 310 nm was also observed. The band at 310 nm corresponds probably to the 6s→6p transition of $Bi^{3+}$ ion. From the emission spectra under 220 nm excitation (curve a' and b' in Fig. 3), we have observed that the emission band of $YNbO_4$ shifts to longer wavelength by $Bi^{3+}$ doping (curve b'). Blasse and Bril[8] have also reported these characteristic phenomena.

Under 310 nm excitation, we have observed that the emission band of Bi-doped $YNbO_4$ shifts to even longer wavelength peaking at 440 nm (curve b" in Fig. 3). Considering that the excitation of 310 nm is due to introducing $Bi^{3+}$, we can ascribe the emission band at 440 nm to $Bi^{3+}$ only. Under 220 nm excitation, the emission from both host Nb-O and dopant $Bi^{3+}$ are possible in $YNbO_4$:Bi. Therefore the curve b' in Fig. 3 can be split into two emission peaks. We have done gaussian fitting on the curve b', which is was separated into two peaks at 394 nm and 438 nm, which agree well with the host peak ( curve a') and the $Bi^{3+}$ peak ( curve b" ) in Fig. 3, respectively. We have separated the PL emission peaks under 220 nm excitation for various Bi concentration and found that the contribution from $Bi^{3+}$ peak is getting bigger as more Bi is doped. It explains that the emission peak position of Bi-doped $YNbO_4$ (curve b') shifts to longer wavelengths as Bi concentration increases.[2,9]

From the calculated PDOS, we can predict absorption edge of $YNbO_4$. Even though we were not able to measure absorption edge directly from our experiment, we can estimate it from the excitation spectra. For $YNbO_4$, the absorption edge is estimated as 4.5eV (275 nm) from Fig. 3. It corresponds to the CT band gap of $YNbO_4$, which has been calculated as 4.2 eV (295 nm). When Bi is doped in $YNbO_4$, there is another excitation peak of which absorption edge is estimated as 3.6 eV (344 nm) in Fig. 3. From the calculated PDOS of Bi-doped $YNbO_4$, the energy difference of Bi 6s and 6p is 3.4 eV (364 nm), which corresponds to the second absorption edge. Since PDOS of Bi 6s overlapped with PDOS of O 2p, the excitation can occur not only via transition from Bi 6s to 6p but also via the charge transfer from O 2p to Bi 6p. In the same context, the emission under 310 nm can be ascribed to both Bi-O charge transfer and internal transition of Bi. Considering the broad shape of the curve b" in Fig. 3, it is more like charge transfer emission band from Bi-O. From the calculations and experiment, we can conclude that the excitation and emission by introducing Bi have both transition characters, i.e. the transition inside Bi electronic energy levels and the transition between Bi and O via charge transfer.

## Summary

The $YNbO_4$ and $YNbO_4$:Bi phosphors were prepared using solid state reaction method and the optimum conditions of preparation for maximum CL emission intensity was determined. Their PL excitation and emission spectra were measured. The separation of Bi effect on emission spectra was possible from the two different excitations ( 220 nm and 310 nm ). From the calculations, we can confirm the charge transfer gap between Nb 4d and O 2p of host material $YNbO_4$. For Bi-doped $YNbO_4$, the calculated PDOS shows Bi 6s and O 2p PDOS are overlapped. Therefore the extra peak at 310 nm of excitation spectra is probably originated from both Bi 6s → 6p transition and Bi-O charge transfer transition. These two transitions also cause the emission peak shift to longer wavelength in $YNbO_4$:Bi. From this study, we can determine the optimized conditions for CL and theoretical luminescence mechanism of $YNbO_4$ and $YNbO_4$:Bi phosphors as a potential application for FED.

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