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Optical Excitation and Emission Spectra of $YNbO_4 : Eu^{3+}$

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Abstract : In the excitation spectra of $YNbO_4 : Eu^{3+}$, the charge transfer (CT) band around 270 nm due to $[NbO_4]^{3-}$-Eu^{3+} interaction and sharp excitation peaks by f-f transition of Eu^{3+} strongly appeared simultaneously. CT band depended on the structural properties of powders, showing the red-shift with increasing the crystallinity, while the f-f transition peaks were independent of the crystallinity. For $YNb_{1-x}Ta_xO_4 : Eu^{3+}$ (x = 0.05–0.2), $[TaO_4]^{3-}$ configuration was locally constructed, leading to the blue-shift in CT band and the decrease in the red emission intensity with increasing the Ta content.

Keywords : Photoluminescence, $YNbO_4$, Charge transfer, Europium

1. Introduction

$YNbO_4$ powders have been known not only as blue emitting materials around 405 nm under 260 nm excitation, but also as x-ray phosphors of which spectra exhibit high energy emissions around 256 nm.[1)] Niobium containing-$YTaO_4$ can efficiently convert x-ray to a visible light of 410 nm, resulting in higher luminescent properties than $CaWO_4$.[2,3)]

The substitution of rare-earth (RE) ions for yttrium atoms enables $YNbO_4$ to emit visible lights under the excitation of the charge transfer (CT) band that generated from the energy transfer between $[NbO_4]^{3-}$ and RE ions. In case of $YNbO_4 : Eu^{3+}$, $[NbO_4]^{3-}$ can be self-activated by UV, and then the absorbed energy is efficiently transferred to Eu^{3+} ions by a non-radiative CT mechanism, showing CT band around 270 nm. This CT band excitation causes the red-light emissions corresponding to $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3…) transitions of Eu^{3+}. With increasing Eu^{3+} concentration, the red emission intensity by CT band excitation increases, while simultaneously the blue-emission due to self-activated $[NbO_4]^{3-}$ excitation is quenched.[1,4)] In addition to CT band, sharp peaks of f-f transitions of Eu^{3+} around near UV range can be observed.

$YNbO_4$ has polymorphism of the high temperature T-phase (T-scheelite, $I4_{1/a}$) and the low temperature monoclinically distorted M-phase (M-fergusonite, C_2). The transition temperature between two phases is 500-800°C depending on RE ions.[2,5-8)] $YNbO_4$ phosphors have been synthesized by a solid-state reaction,[9-13)] a firing of citrate complexes,[14,15)] and a pyrolysis of metal-alkoxide.[16)]

In spite of some previous works on the luminescent properties of $YNbO_4 : Eu^{3+}$, the correlations between the micro-structural changes and the luminescent properties (CT and f-f transition of Eu^{3+}) have not been reported in detail yet. In this work, we prepared $YNbO_4 : Eu^{3+}$ powders by a flux method, and then investigated the optical excitation and emission properties of Eu^{3+} in $YNbO_4$.

2. Experiment

Y_2O_3, Nb_2O_5, Ta_2O_5, and Eu_2O_3 powders were used as starting materials. H_3BO_3, LiCl, and NH_4Cl were added as a flux, respectively to facilitate the solid-state reactions and enhance the luminescent properties by accelerating the kinetics of the formation of the desired compounds. According to our preliminary experiment, LiCl among the flux was superior to the others in a single phase formation and luminescence. After ball-milling the mixtures for 24 hours, they were fired at 1000-1400°C flowing 30 sccm N_2 gas for 12 hours in an electric tube furnace. The temperature was

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raised by 5°C/min. The crystalline phases of prepared powders were determined by XRD (X-ray diffractometer, SIEMENS D5005) using CuK_{α} radiation (λ = 1.5406 Å). PL (Photoluminescence) properties were measured at room temperature by PL (PSI Darsa 5000) system using a xenon lamp as an excitation source.

3. Results and Discussion

XRD patterns of $0.95Y_2O_3$-$1.0Nb_2O_5$-$0.05Eu_2O_3$-LiCl (7 wt%) mixture prepared as a function of the firing temperature are shown in Fig. 1. M-$YNbO_4$ formation can be completed by the reaction schemes (1) and (2).

$$Y_2O_3{=}Nb_2O_5 + 2LiCl \xrightarrow{\text{Low Temperature}} 2YOCL + 2LiNbO_3 \quad (1)$$

$$2YOCl + 2LiNbO_3 \xrightarrow{\text{High Temperature}} 2YNbO_4 + 2LiCl \quad (2)$$

Since $LiNbO_3$ phase was not achieved at all temperature ranges as shown in Fig. 1, it could be thought that the lowest temperature of 1000°C was already high enough to follow the reaction scheme (2) process. At 1000°C, $YNbO_4$ and the secondary phase of Y_3NbO_7 weakly appeared. With increasing the temperature, XRD peaks of $YNbO_4$ gradually increased, while those of Y_3NbO_7 weakened, resulting in a single phase $YNbO_4$ above 1300°C.

The related excitation spectra are shown in Fig. 2. The broad band around 270 nm corresponded to the charge transfer (CT) between $[NbO_4]^{3-}$ and Eu^{3+} emitting level, while the other sharp bands were assigned to f-f transitions in Eu^{3+} $4f^6$ configuration, among which $^7F_0 \rightarrow {}^5L_6$ at 397 nm was the most significant and $^7F_0 \rightarrow {}^5L_7$ at 385 nm was also comparatively strong. With increasing the temperature, CT band intensity gradually increased up to 1300°C, and then slightly dropped at 1400°C, furthermore the peak shifted to the longer wavelength (the red-shift), saturating at 1400°C. On the other hand $^7F_0 \rightarrow {}^5L_6$ transition continuously increased up to 1400°C in intensity without a shift of the peak position. CT band closely depends on the micro-structural changes of a host material, because its properties are mainly ascribed to the efficiency of the energy transfer from $[NbO_4]^{3-}$ to Eu^{3+} ions. So a correlation between CT band and the crystallinity of $YNbO_4$ was investigated. Full width of half maximum (FWHM) values of (021) peak in Fig. 1 and the peak wavelength of CT band are shown in Fig. 3. With increasing the temperature, FWHM values continuously decreased and then a little increased at 1400°C. This meant that the crystallinity continuously developed up to 1300°C, but slightly deteriorated at 1400°C due to the excess high temperature. The higher crystallinity caused the stronger interaction of $[NbO_4]^{3-}$-Eu^{3+}, namely the easier electron transition from $[NbO_4]^{3-}$ to Eu^{3+} energy level, leading to the red-shift and the increase

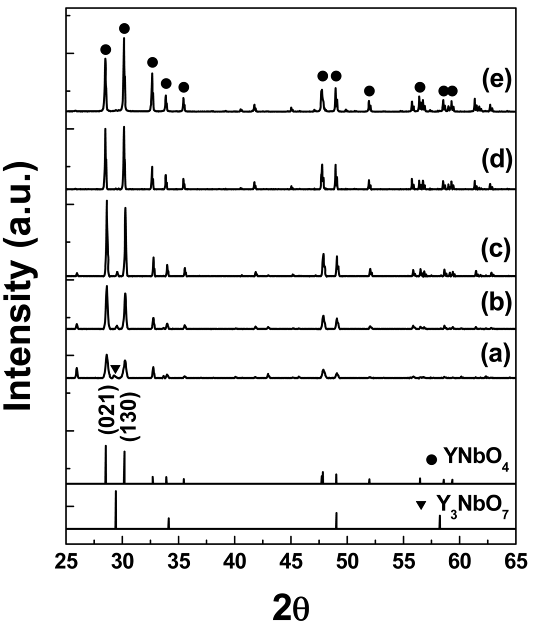

Fig. 1. XRD patterns of $0.95Y_2O_3$-$1.0Nb_2O_5$-$0.05Eu_2O_3$-LiCl (7 wt%) mixture prepared as a function of the firing temperature. (a) 1000°C, (b) 1100°C, (c) 1200°C, (d) 1300°C, and (e) 1400°C.

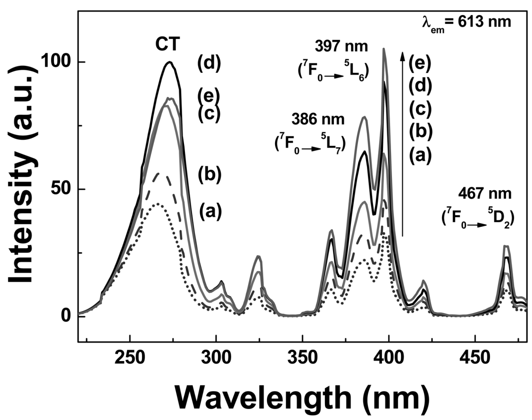

Fig. 2. PL excitation spectra of $YNbO_4 : 0.1Eu^{3+}$ fired at various temperatures. (a) 1000°C, (b) 1100°C, (c) 1200°C, (d) 1300°C, and (e) 1400°C.

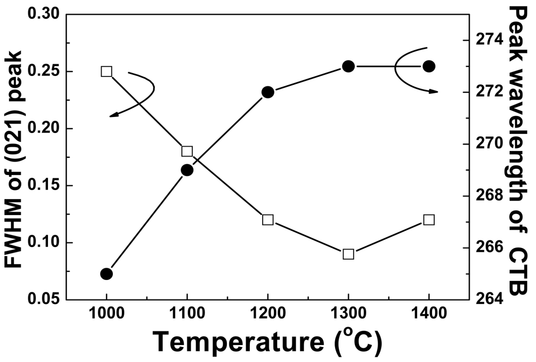

Fig. 3. FWHM of (021) peak and peak wavelengths of CT band as a function of the firing temperature.

of the peak intensity. However, at 1400°C the red-shift was suppressed and the intensity decreased due to the high firing temperature where FWHM a little increased. As shown in Fig. 2, the peak of $^7F_0 \rightarrow {}^5L_6$ transition at 397 nm continuously increased up to 1400°C without the peak shift, indicating that it was independent of the crystal structure unlike CT band.

PL emission spectra excited by CT band are shown in Fig. 4. Typical Eu^{3+} red emissions assigned to $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2….) transition of Eu^{3+} ions were observed, and $^5D_0 \rightarrow {}^7F_2$ at 613 nm was dominant. The inset in Fig. 4 exhibits a variation of PL intensity as a function of the firing temperature under CT band and 397 nm excitation, respectively. The increase of the temperature caused the enhancement of the red emission, and the emission behaviors at 1400°C well coincided with the variations of the excitation spectra in Fig. 2. Namely, at 1400°C the emission intensity due to CT band saturated, while that by 397 nm excitation continuously increased.

To investigate the effects of the cation substitution in the tetrahedral niobate, PL excitation spectra of $YNb_{1-x}Ta_xO_4 : Eu^{3+}$ (x = 0-0.2) were measured and resulting variations are shown in Fig. 5. With increasing the Ta content from 0.05 to 0.2, the excitation intensity of CT bands gradually decreased and the peak wavelength shifted to shorter wavelengths (the blue-shift). The crystal structure of $YTaO_4$ is very similar to that of $YNbO_4$, but it has, besides T- and M-type, another M'-type,[3,17] which can be synthesized at the low tem perature below 1400°C and is used as a luminescent material. Both Nb and Ta atoms are located in a distorted octahedral coordination in M-$YNbO_4$ and M'-$YTaO_4$, respectively, of which CT bands due to tantalate

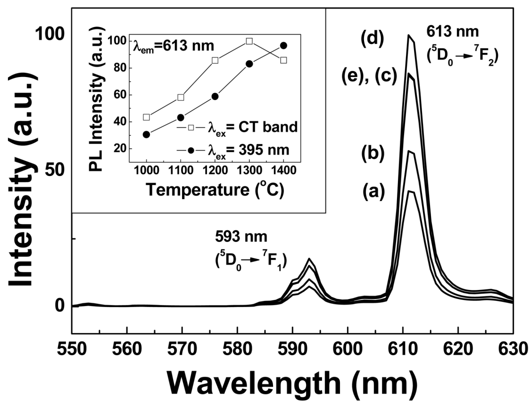

Fig. 4. PL emission spectra of $YNbO_4 : 0.1Eu^{3+}$ fired at various temperatures. (a) 1000°C, (b) 1100°C, (c) 1200°C, (d) 1300°C, and (e) 1400°C.

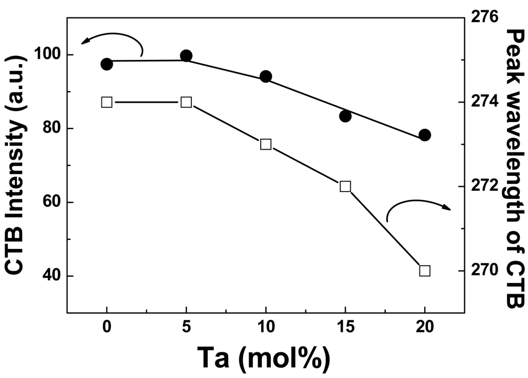

Fig. 5. The variation of the excitation intensity and the peak wavelength of CT band of $YNb_{1-x}Ta_xO_4 : Eu^{3+}$.

$[TaO_4]^{3-}$-Eu^{3+} and niobate $[NbO_4]^{3-}$-Eu^{3+} are shown around 254 nm[18] and 270 nm, respectively. M'-$YTaO_4$ phase did not appear in XRD, so the substituted Ta atoms certainly formed the $[TaO_4]^{3-}$ coordination partially in M-$YNbO_4$, but the secondary M'-$YTaO_4$ phase was not created. X. Xiao *et al.* reported that $[TaO_4]^{3-}$ could not exhibit a self-emission in europium doped $YNb_yTa_{1-y}O_4$ (y = 0.1-0.9) system, because the efficiency of the transfer from $[TaO_4]^{3-}$ to $[NbO_4]^{3-}$ was high and the emission of $[NbO_4]^{3-}$ overlapped that of $[TaO_4]^{3-}$.[19] G. Blass et al. demonstrated that niobium-containing tantalates yielded mainly niobate emission due to efficient energy transfer.[20] However their results did not show the blue-shift in CT band unlike ours. Conclusively, it could be speculated that the local $[TaO_4]^{3-}$ coordination in $YNbO_4$ did not contributed to CT directly, but made the interaction of $[NbO_4]^{3-}$

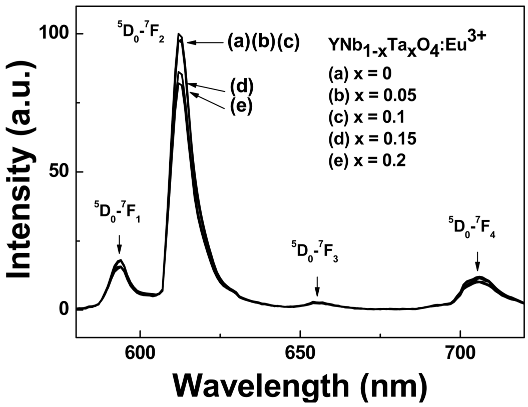

Fig. 6. The emission spectra of of $YNb_{1-x}Ta_xO_4 : Eu^{3+}$. (a) x = 0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.15, and (e) x = 0.2

-Eu^{3+} weaker by distorting the crystal field, leading to the blue-shift and the decrease of CT band intensity.

Corresponding PL emission spectra are shown in Fig. 6. At all x values the strongest peak appeared at 613 nm, corresponding to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}, while the weak peaks at 593, 655, and 705 nm assigned to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ were also observed, respectively. It is known that in low symmetric crystal lattices, the strongest emission peak is assigned to $^5D_0 \rightarrow {}^7F_2$ transition, so our emission spectra revealed that all Eu^{3+} ions occupied the asymmetric C_2 sites of Y^{3+} in $YNb_{1-x}Ta_xO_4$. At x = 0-0.1, the emission intensities were almost same, and then significantly dropped at 0.15-0.2. X. Xiao *et al.* concluded in their report that, in $YNb_yTa_{1-y}O_4 : Eu^{3+}$ (y = 0.1-0.9), the shift of $^5D_0 \rightarrow {}^7F_1$ emission peak at 593 nm and the decrease of the symmetry with increasing the niobium content were attributed to the phase change, which meant the coexistence of M-$YNbO_4$ and M'-$YTaO_4$ phases.[19] In contrast to their work, the shift of $^5D_0 \rightarrow {}^7F_1$ emission peak was not observed in our work, and also M'-$YTaO_4$ phase did not appeared in XRD. This discrepancy might be caused by the different experimental range of Nb/Ta ratio. A cation ratio of Ta/(Nb+Ta) in our work was so small (≤ 0.2) that M'-$YTaO_4$ phase could not be created, while that in Xiao's work was large (≤ 0.9), leading to the appearance of M'-$YTaO_4$ phase. From the excitation and emission spectra it could be summarized that $[TaO_4]^{3-}$ configuration was locally constructed in $YNb_{1-x}Ta_xO_4 : Eu^{3+}$ system, which distorted the crystal field surrounding Eu^{3+} and weakened $[NbO_4]^{3-}$-Eu^{3+} interaction, resulting in the blue-shift in CT band and the decrease of red emissions with increasing the Ta content.

4. Conclusion

$YNbO_4 : Eu^{3+}$ powders were synthesized by a flux method using LiCl. The excitation spectra exhibited not only the broad peak around 270 nm due to CT band between $[NbO_4]^{3-}$ and Eu^{3+} emitting level, but also the sharp peaks by f-f transitions of Eu^{3+} ions among which $^7F_0 \rightarrow {}^5L_6$ at 397 nm appeared as the strongest one. With increasing the firing temperature, CT band exhibited the red-shift due to the improved crystallinity, while the peaks of f-f transition including $^7F_0 \rightarrow {}^5L_6$ did not shift regardless of the crystallinity. In $YNb_{1-x}Ta_xO_4 : Eu^{3+}$ system, locally constructed $[TaO_4]^{3-}$ configuration led to the blue-shift in CT band and the decrease of red emissions with increasing the Ta content.

Acknowledgment

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