Energy transfer in Dy$^{3+}$ and Al$^{3+}$ co-doping ZnNb$_2$O$_6$

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Abstract. Dy$^{3+}$, Al$^{3+}$ codoping ZnNb$_2$O$_6$ phosphors were synthesized by solid state reaction. The luminescence intensity of ZnNb$_2$O$_6$:xDy$^{3+}$(0.02$\leqslant$x$\leqslant$0.13) can be enhanced by codoping with Al$^{3+}$ under 365 nm excitation, but weakened under 254 nm excitation, because energy can be transferred from CTS to the excitation states of Dy$^{3+}$. The results indicate that under 365 nm excitation the relative intensities of the peaks at 490 nm and 575 nm were varied with the increase of Al$^{3+}$ content, this phenomenon causes the movement of chromaticity coordinates from the white to the yellow side, and could be helpful for developing new LEDs phosphors.

1. Introduction

Nowadays, the versatility of luminescent materials have attracted researchers’ attention, because of their application in various fields, e.g., fluorescent lamps, display devices, detector systems, immunoassays, and scintillates of phosphor marking [1-4]. In these devices, luminescent materials absorb the energy and then convert it to visible light.

As interesting photoactive host materials, the luminescent properties of niobates have been studied extensively by many researchers, e.g., LiNbO$_3$ [5-7], KNbO$_3$ [8,9], LnNbO$_4$ (Ln= Pr, La, Ga, and Y) [10,11], KLaNb$_2$O$_7$ [12], Sr,Ba$_{1-x}$Nb$_2$O$_6$ [13,14], and Ba$_5$Nb$_4$O$_{15}$ [15]. Zinc niobate (ZnNb$_2$O$_6$, ZN) with a columbite crystal structure has been known as one of binary niobate compounds with excellent dielectric properties at microwave frequencies: $Q \times f = 87300$ GHz, $\varepsilon_r = 25$ and $\tau_f = -56$ ppm/$^\circ$C [16-19]. It has very low loss and high dielectric constant, thus is a promising candidate for applications in microwave devices [20-22].

Dy$^{3+}$ ion is a good activator for preparation of electron-trapping luminescence materials. Defects and traps could be produced by substitution of the divalent alkaline-earth ions in the matrix with trivalent Dy$^{3+}$ ion or by high-energy radiation. Electrons or holes could be trapped by these defects, then the electrons and holes recombine, and light will emit by radiation released from traps with different wavelength.

Dy$^{3+}$ has two dominant emission bands in the emission spectra in many host matrixes such as Ba$_3$Gd(PO$_4$)$_3$, Mg$_2$Gd$_8$(SiO$_4$)$_6$O$_2$ and SrB$_4$O$_7$ [23-26]. The band located at 574 nm (yellow) attributes to the hypersensitive transition $^4F_{9/2} \rightarrow ^4H_{13/2}$ ($\Delta L = 2$, $\Delta J = 2$), and another band located at 487 nm (blue) corresponds to the transition $^4F_{9/2} \rightarrow ^4H_{15/2}$. The intensity of the former varies along with the environment more obviously than that of the latter. In the CIE 1931 chromaticity diagram, the line linking the yellow with blue wavelength crosses the white light region; therefore, by adjusting a suitable yellow-
to-blue intensity ratio (Y/B), the chromaticity coordinates of the phosphor doped with Dy\(^{3+}\) ions could be controlled in the white region. There are several reports about the phosphors doping with Dy\(^{3+}\) ions, which were studied for direct white light production [23-27]. Furthermore, the codoping Al\(^{3+}\) may be beneficial in enhancing the luminescent intensity of phosphor [28,29]. In this work, the photoluminescence (PL) of ZnNb\(_2\)O\(_6\):Dy\(^{3+}\) codoped with Al\(^{3+}\) evaluated under the excitation of ultraviolet (UV) was investigated.

2. Experimental:
Powder samples ZnNb\(_2\)O\(_6\):\(x\)Dy\(^{3+}\) (0.02 \(\leq x \leq 0.13\)) and ZnNb\(_2\)O\(_6\):0.09Dy\(^{3+}\),\(y\)Al\(^{3+}\) (0.02 \(\leq y \leq 0.13\)) were prepared by solid state reactions. The purities of ZnO and Nb\(_2\)O\(_5\) are analytical reagent (AR), and that of Dy\(_2\)O\(_3\) and Al\(_2\)O\(_3\) is better than 99.99%. The doping amount \(x\) of Dy\(_2\)O\(_3\) is from 0 to 13%, and the same to that of Al\(_2\)O\(_3\). Stoichiometric amounts of the starting reagents ZnO, Nb\(_2\)O\(_5\), Dy\(_2\)O\(_3\), and Al\(_2\)O\(_3\) were thoroughly mixed and ground together. The mixture was heated at 1000°C for 4 h and cooled to room temperature subsequently.

The powder X-ray diffraction (XRD) patterns of all samples were carefully collected in the \(2\theta\) range 10–80° (Rigaku D/MAX-2400 X-ray diffractometer with Ni-filtered Cu K\(\alpha\) radiation). The luminescence spectra were recorded on a FLS-920T fluorescence spectrophotometer with Xe 900 (450 W xenon arc lamp) as the light source. All the spectra were recorded at room temperature.

3. Results and discussion:
The XRD patterns of the samples ZnNb\(_2\)O\(_6\):\(x\)Dy\(^{3+}\),\(y\)Al\(^{3+}\) are shown in Fig. 1 (a) and (b), through indexed by orthorhombic structure, those were proved as single phase, in line with the JCPDS card 76-1827.

![Figure 1](image-url)

Figure 1. (a). The X-ray powder diffraction patterns of ZnNb\(_2\)O\(_6\):\(x\)Dy\(^{3+}\); (b). The X-ray powder diffraction patterns of ZnNb\(_2\)O\(_6\):0.09Dy\(^{3+}\),\(x\)Al\(^{3+}\).

It is well known that the host lattice ZnNb\(_2\)O\(_6\) crystallizes in the orthorhombic symmetry with space group Pbcn (60), through analyzing XRD, it can be calculated that \(a=14.2527\) Å, \(b=5.7170\) Å and \(c=5.0378\) Å. Fig. 2 shows the crystal structure of ZnNb\(_2\)O\(_6\). Along the \(a\)-axis, the layers of Zn\(^{2+}\) and Nb\(^{5+}\) are separated by planes of O\(^2-\). The ZnO\(_6\) and NbO\(_6\) octahedra are connected by common corners, and each NbO\(_6\) octahedron is linked with six ZnO\(_6\) octahedron, each ZnO\(_6\) octahedron is linked with three ZnO\(_6\) octahedron and three NbO\(_6\) octahedron, the NbO\(_6\) and ZnO\(_6\) are edge-shared groups.
Figure 2. The crystal structure of ZnNb$_2$O$_6$

Figure 3 shows several emission spectra of ZnNb$_2$O$_6$:\textit{x}Dy$^{3+}$ under 254 nm excitation. From Fig. 3, the peaks at 490 nm and 575 nm are observed and could be attributed to $^4$F$_{9/2}$-$^6$H$_{15/2}$, $^4$F$_{9/2}$-$^6$H$_{13/2}$ transitions of Dy$^{3+}$ ion. It’s obvious that the intensities of the peaks at 490 nm and 575 nm are gradually enhanced along with $x$ increasing and become dominant when $x=0.09$, then weakened when $x>0.09$.

Figure 4. The emission spectra of ZnNb$_2$O$_6$:\textit{x}Dy$^{3+}$(0.02 $\leq x \leq 0.13)$ ($\lambda_{ex}=365$ nm)

Several emission spectra of ZnNb$_2$O$_6$:\textit{x}Dy$^{3+}$ and ZnNb$_2$O$_6$:0.09Dy$^{3+}$\textit{x}Al$^{3+}$ under 365 nm excitation are shown in Figure 4 and 5, respectively. The emission peaks at 490 nm and 575 nm are observed, which could be also attributed to $^4$F$_{9/2}$-$^6$H$_{15/2}$, $^4$F$_{9/2}$-$^6$H$_{13/2}$ transitions of Dy$^{3+}$ ion. It’s obvious that the intensities of the peaks at 490 nm and 575 nm are gradually enhanced along with $x$ increasing and become dominant when $x=0.09$, then weakened when $x>0.09$ in the two figures, however, doping Al$^{3+}$ ions can enhance the intensity of luminescence effectively and the intensity of dominant emission peak of ZnNb$_2$O$_6$:0.09Dy$^{3+}$0.09Al$^{3+}$ could be enhanced as 3.15 times stronger than that of
ZnNb$_2$O$_6$:0.09Dy$^{3+}$, so that it’s a potential LED phosphors. As we know, the increase in the Dy$^{3+}$ or Al$^{3+}$ concentration too much would cause a cross-relaxation process between neighboring Dy$^{3+}$ ions, leading to quenching of the emission. Y. H. Wang et al, have reported that the luminescence intensity could be enhanced by doping with less Al$^{3+}$ ions [28,29]. But in Figure 6, the intensity of dominant emission peak of ZnNb$_2$O$_6$:0.09Dy$^{3+}$ 0.09Al$^{3+}$ is much weaker than that of ZnNb$_2$O$_6$:0.09Dy$^{3+}$ under 254 nm excitation, that is opposite to Figure 5.

Figure 5. The emission spectra of ZnNb$_2$O$_6$:0.09Dy$^{3+}$ xAl$^{3+}$ (0.02 $\leq$ x $\leq$ 0.13) ($\lambda$$_{ex}$=365 nm)

Figure 6. The emission spectra of ZnNb$_2$O$_6$:0.09Dy$^{3+}$ 0.09Al$^{3+}$ and ZnNb$_2$O$_6$:0.09Dy$^{3+}$ ($\lambda$$_{ex}$=254 nm)

Figure 7 shows the excitation spectra of ZnNb$_2$O$_6$:0.09Dy$^{3+}$ 0.09Al$^{3+}$ and ZnNb$_2$O$_6$:0.09Dy$^{3+}$ with the emission at 575 nm. In the excitation spectrum, it’s obvious observed that there is a strong absorption band near 270 nm, that can be attributed to the charge transfer band (CTS) between O$^{2-}$ and Dy$^{3+}$ ions. It is obviously exhibited that the CTS became littler narrower than another and had a little bathochromic shift when codoping with Al$^{3+}$. In the range of 320 nm-470 nm, the absorption is enhanced by coding with Al$^{3+}$, the series of line spectra in this range are ascribed to the transitions from the ground state to excitation states in the 4f$^6$ configuration of Dy$^{3+}$ ions. The peaks at 327 nm, 354 nm, 367 nm, 384 nm, 426 nm and 454 nm are attributed to $^4$H$_{15/2}$$^4$K$_{15/2}$, $^4$H$_{15/2}$$^4$M$_{15/2}$, $^6$H$_{15/2}$$^4$P$_{3/2}$, $^6$H$_{15/2}$$^4$M$_{1/2}$, $^6$H$_{15/2}$$^4$G$_{1/2}$ and $^6$H$_{15/2}$$^4$I$_{15/2}$ transitions of Dy$^{3+}$ respectively. The radii of Zn$^{2+}$, Nb$^{5+}$ and Al$^{3+}$ ions are 0.74 Å, 0.64 Å and 0.51 Å, and the radius of Al$^{3+}$ ions is more close to that of Nb$^{5+}$ ions, thus sites of Nb$^{5+}$ could be more probably occupied by Al$^{3+}$ ions. In addition, the electronegativity of Al$^{3+}$ ions is little bigger than that of Nb$^{5+}$ ions. It’s obviously showed in figure 2 that Nb$^{5+}$ and Zn$^{2+}$ ions are connected with O$^{2-}$ ions, when codoping with Al$^{3+}$ ions in Nb$^{5+}$ sites, the covalence of Dy$^{3+}$ ions at Zn$^{2+}$ sites and O$^{2-}$ ions increases, thus the energy difference for electrons transition between the two ions become smaller, CTS between the two ions moves to lower energy location. Thus when doping with a few Al$^{3+}$ ions, it’s more easily transfering energy from CTS to the excitation states of Dy$^{3+}$ by relaxation effect.

Figure 8 presents the chromaticity coordinates (x, y) of ZnNb$_2$O$_6$:0.09Dy$^{3+}$ xAl$^{3+}$ excited under 365 nm in the CIE 1931 chromaticity diagram. The blackbody radiation locus is indicated by the solid curve. It is obvious that the chromaticity coordination of ZnNb$_2$O$_6$:0.09Dy$^{3+}$ xAl$^{3+}$ gradually moves to the warm-white side and approaches the yellow region with increasing x, then x>0.09 move to the opposite direction.
4. Conclusions

The luminescence property of ZnNb$_2$O$_6$:xDy$^{3+}$,yAl$^{3+}$ phosphor was investigated under UV excitation. Through an analysis of the luminescence spectra, it is obvious that energy can be transferred from CTS to excitation states of Dy$^{3+}$ ions by codoping with Al$^{3+}$ ions, the peaks located in the range 320 nm-470 nm is accordingly enhanced in the excitation spectra. Thus the emission peaks can be enhanced under 365 nm excitation and the relative intensity variety of main emission peaks at 490 and 575 nm make the results in the movement of the chromaticity coordinates from the cold-white to the warm-white side by codoping with Al$^{3+}$ ions. In other words, through varying the amount of x, the chromaticity coordinates of ZnNb$_2$O$_6$:0.09Dy$^{3+}$ $x$Al$^{3+}$ can be expediently adjusted, thus ZnNb$_2$O$_6$:0.09Dy$^{3+}$ 0.09Al$^{3+}$ is a potential LED phosphors.

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