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Photoluminescence and Structural Characteristics of Eu-doped ZnO–Li_3NbO_4

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In this study, Eu^{3+}-doped ZnO–Li_3NbO_4 phosphors were prepared by the sol–gel method. The physical and luminescence properties of the Eu^{3+}-doped ZnO–Li_3NbO_4 structure were characterized. The results show the crystallinity of the biphasic ZnO–Li_3NbO_4 structure sintered at temperatures above 400 °C. The main excitation and emission bands of the Eu^{3+}-doped ZnO–Li_3NbO_4 phosphors were 466 nm ($^7F_0 \rightarrow {}^5D_2$) and 615 nm ($^5D_0 \rightarrow {}^7F_2$), respectively. When the amount of Eu^{3+} was 5%, the highest emission intensity was obtained at 595 nm ($^5D_0 \rightarrow {}^7F_1$) and 615 nm ($^5D_0 \rightarrow {}^7F_2$).

1. Introduction

Zinc oxide–lithium niobate (ZnO–Li_3NbO_4) has become a popular material for application in nonlinear optical and optoelectronic devices.[1,2] The use of a biphasic ceramic material plays an important role in optical or biomedical applications. For example, Fariña *et al.*[3] studied biphasic calcium phosphate ceramics for biomedical and implanted applications. Bernardeschi *et al.*[4] studied granules of biphasic ceramics for the rehabilitation of canal walls.

Among rare-earth-doped materials, Eu^{3+} attracts considerable scientific attention. The intra-4f-shell transitions of Eu^{3+} show that the excited levels shift the lower energy levels of $^5D_0 \rightarrow {}^7F_j$ (j = 1, 2, 3, 4).[5,6] The optical properties of Eu^{3+}:ZnO nanophosphors are important in material applications such as the fabrication of electroluminescence devices and biolabels.[7] Ningthoujam *et al.* studied ZnO nanoparticles with and without Li^+ and Eu^{3+} ions at low temperatures and their luminescence properties.[7] Red luminescence was observed in the wavelength range of 610–620 nm.[8,9] ZnO–Li_3NbO_4 crystals exhibit a second phase structure and could be used as a capacity rare-earth-doped host material. However, there are only a few reports on the structure and luminescence of ZnO–Li_3NbO_4 prepared by the sol–gel method.

In the present study, we synthesized Eu^{3+}-doped ZnO–Li_3NbO_4 by the sol–gel method and examined its structural, optical absorption, and photoluminescence properties.

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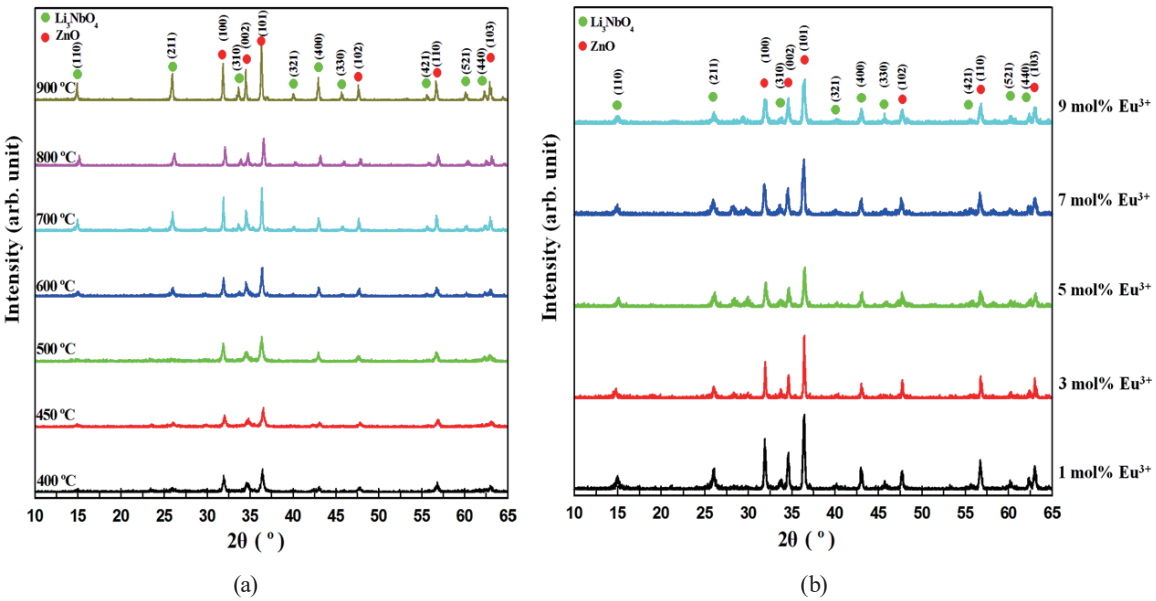
2. Experiments

ZnO–Li_3NbO_4:Eu powders were prepared by the sol–gel method. 99% zinc nitrate $Zn(NO_3)_2$, 97.7% lithium nitrate ($LiNO_3$), niobium ethoxide $Nb(OC_2H_5)_5$, and 99.8% citric acid (CA) were used as starting materials. First, stoichiometric amounts of $Zn(NO_3)_2$, $LiNO_3$, $Nb(OC_2H_5)_5$, europium nitrate pentahydrate ($Eu(NO_3)_3{\cdot}5H_2O$), and CA were dissolved in distilled (D.I.) water.[10] The precursor was dried in an oven at 150 °C for 2 h. Then, the samples were placed in an Al_2O_3 crucible and then sintered in a furnace at 400–900 °C.

The crystallinity of the samples was measured by X-ray diffraction (XRD, Rigaku D-max/IIB). The microstructure and selected-area electron diffraction (SAED) were characterized by ultrahigh-resolution analytical electron microscopy (HR-AEM, JEOL JEM-2100F CS-STEM). Absorption spectra were obtained using a UV–Vis spectrometer (Jasco V-670 spectrophotometer). The Commission internationale de l'éclairage (CIE) spectrum obtained was analyzed using a photoluminescence (PL, Hitachi F-7000) spectrometer at room temperature.

3. Results and Discussion

Figure 1(a) shows the XRD patterns of ZnO–Li_3NbO_4 synthesized at different sintering temperatures. The crystalline ZnO–Li_3NbO_4 structure was formed gradually over 400 °C (ZnO, JCPDS Card No. 89-0510, unit cell parameters: a, b = 3.249 Å and c = 5.206 Å, and Li_3NbO_4, JCPDS Card No. 75-0907, unit cell parameters: a, b, c = 8.429 Å). The main diffraction peak of 36.26° (101) appeared at different synthesis temperatures. The diffraction peak intensity of ZnO–Li_3NbO_4 with a biphasic polycrystalline structure increased with annealing temperature.



(a) (b)

Fig. 1. (Color online) XRD patterns of ZnO–Li_3NbO_4 synthesized at different (a) sintering temperatures and (b) Eu^{3+} concentrations.

Figure 1(b) shows the XRD patterns of Eu^{3+}-doped ZnO–Li_3NbO_4, whose polycrystalline structure did not change. With increasing Eu^{3+} dopant concentration, the amount of ZnO–Li_3NbO_4 remained the same, which implies that Eu^{3+} can be integrated with a ZnO–Li_3NbO_4 crystal. As the concentration of Eu^{3+} increases above 7%, the crystallinity of the Eu^{3+}-doped ZnO–Li_3NbO_4 is expected to become lower. This phenomenon is mainly caused by structural distortion induced by internal stress.[11]

Figures 2(a)–2(f) show the SEM images of ZnO–Li_3NbO_4 phosphors synthesized by the sol–gel method at different annealing temperatures. The ZnO–Li_3NbO_4 phosphors synthesized at temperatures of 400–700 °C were mostly irregular and agglomerated, and their surfaces were rough. On the other hand, the ZnO–Li_3NbO_4 phosphors synthesized at temperatures of

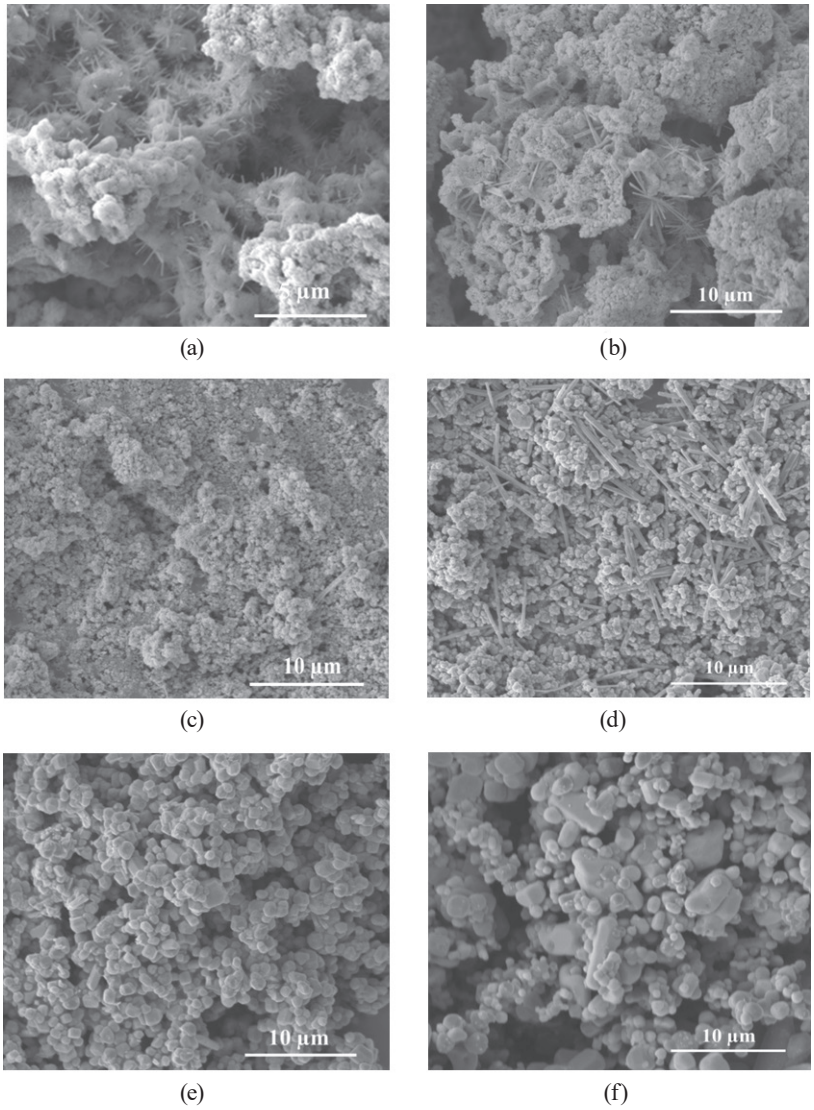
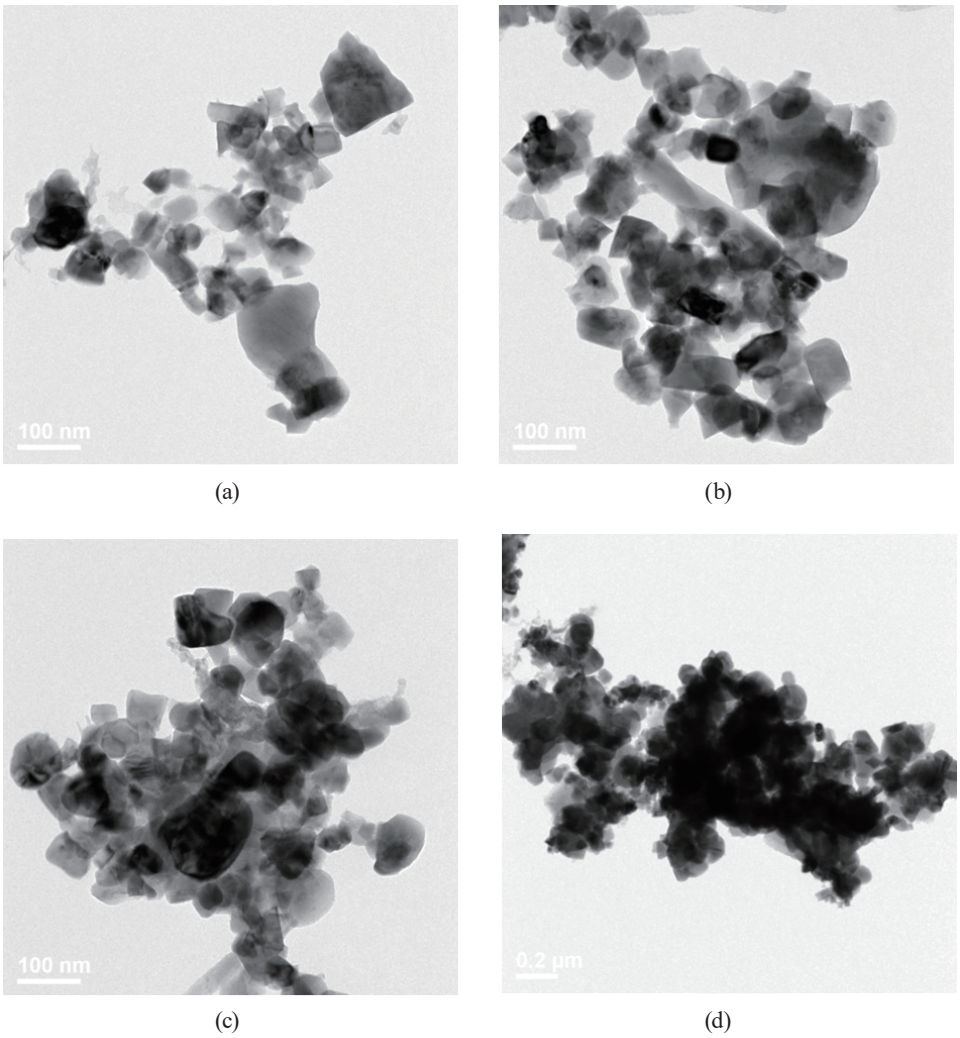


Fig. 2. SEM images of ZnO–Li_3NbO_4 phosphors synthesized at different annealing temperatures: (a) 400, (b) 500, (c) 600, (d) 700, (e) 800, and (f) 900 °C.

800–900 °C showed a similar particle size of about 500 nm and appeared spherical. As the temperature increased, the particle size increased. This was because the high temperature promoted the migration of atoms and the growth of pure grains, affecting the shape of the synthesized ZnO particles forming the films with increasing shape factor.[12] Polygonal Li_3NbO_4 particles were formed by assembling grains with one cubic crystalline phase in the ceramic matrix.[13]

Figures 3(a)–3(d) show the TEM images of ZnO–Li_3NbO_4 phosphors synthesized at different temperatures. When the annealing temperature increased, the stacking and aggregation of ZnO–Li_3NbO_4 particles occurred. Figure 4(a) shows the high-resolution TEM (HR-TEM) image of ZnO–Li_3NbO_4 at an annealing temperature of 900 °C. From the HR-TEM images, the particle size was calculated to be approximately 10–50 nm. Figures 4(b) and 4(c) show the



(a) (b)

(c) (d)

Fig. 3. TEM images of ZnO–Li_3NbO_4 phosphors synthesized at different temperatures: (a) 600, (b) 700, (c) 800, and (d) 900 °C.

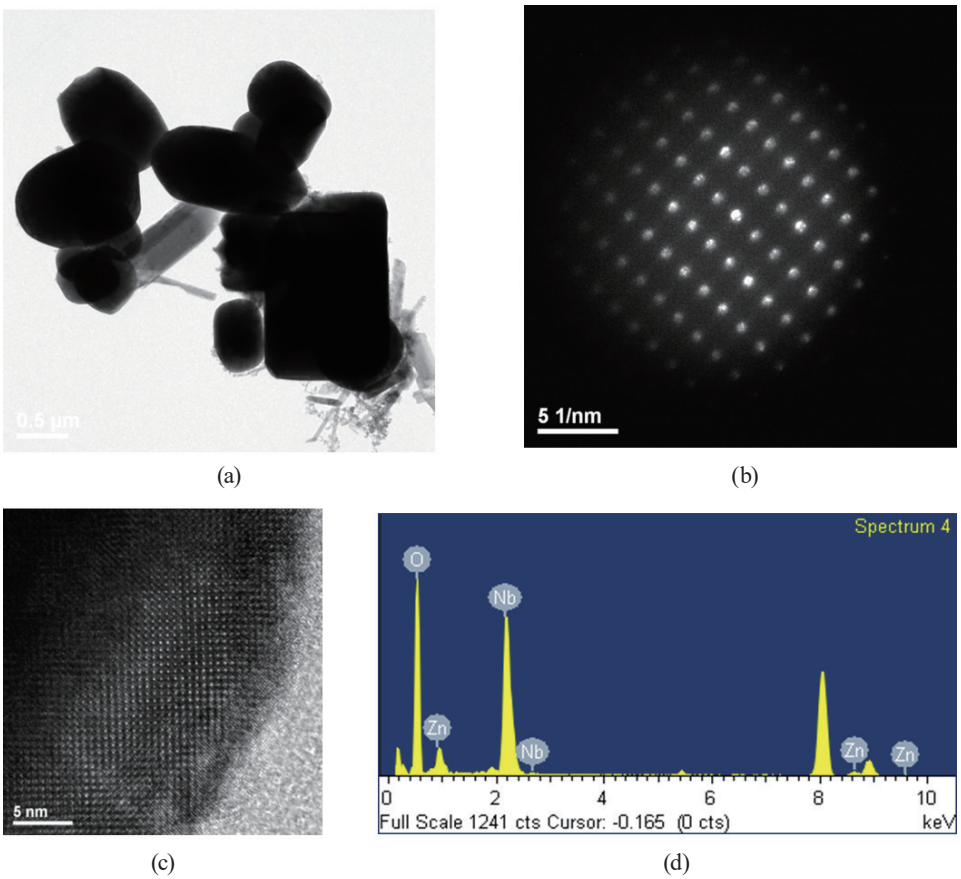


Fig. 4. (Color online) (a) HR-TEM image of pure ZnO–Li_3NbO_4 precursor powders, (b) SAED pattern of ZnO–Li_3NbO_4 annealed at 900 °C for 2 h, (c) electron diffraction pattern, and (d) EDS image.

HR-TEM and SAED patterns of ZnO–Li_3NbO_4, respectively. From the images of the lattice arrangement of ZnO–Li_3NbO_4, it can be seen that the ordering of the lattices is accurate, showing a single complete crystal structure. The lattice size was calculated to be about 0.63 nm. Figure 4(d) shows an energy-dispersive X-ray spectroscopy (EDS) image. EDS results showed the composition of ZnO–Li_3NbO_4.

Figure 5 shows the absorption spectra of ZnO–Li_3NbO_4 doped with 5 mol% Eu^{3+} and annealed at 900 °C for 2 h. The high absorption spectral peak of ZnO–Li_3NbO_4:Eu^{3+} was located between 300 and 400 nm. The absorption spectral peaks at 466 and 538 nm corresponded to $^7F_0 \rightarrow {}^5D_2$ and $^7F_0 \rightarrow {}^5D_1$, respectively. This behavior was attributed to the transition from the $^7F_0$ ground state to the charge transfer state (CTS).[10] The absorption coefficient can be obtained on the basis of the relationship between $(ahv)^2$ and the photon energy[10] as

$$a = \frac{C(hv - E_g)^{1/2}}{hv}, \tag{1}$$

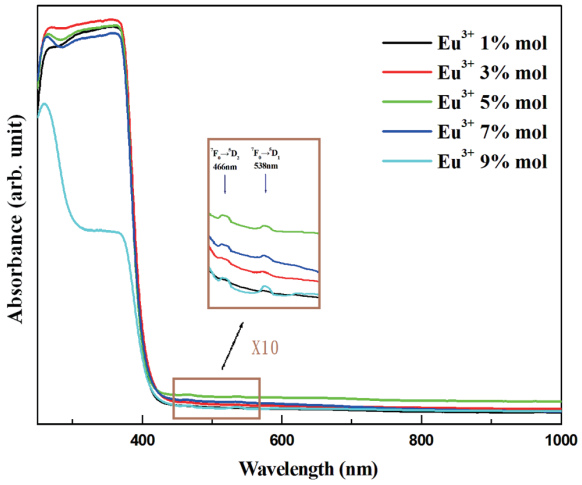
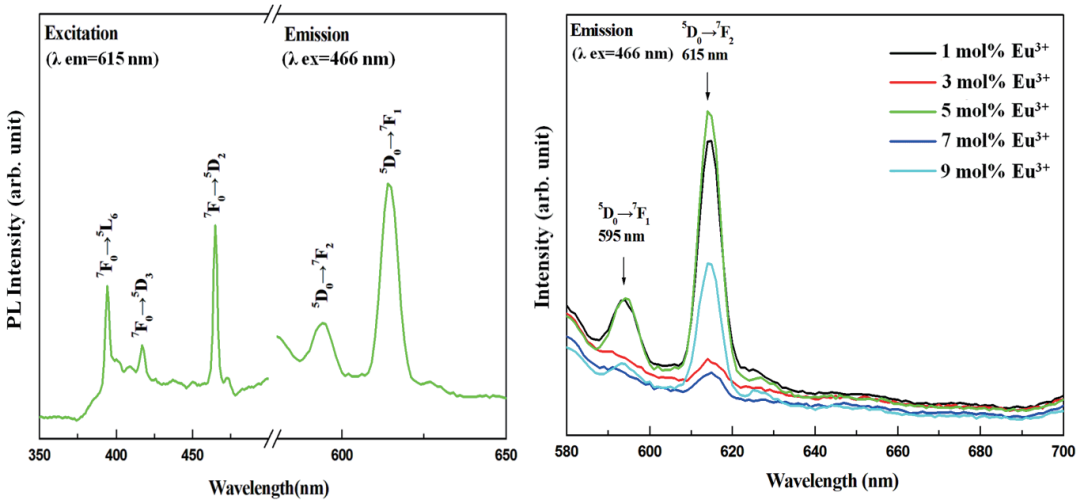


Fig. 5. (Color online) Absorption spectra of ZnO–Li_3NbO_4:$x$$Eu^{3+}$ (x = 1, 3, 5, 7, and 9%).



(a) (b)

Fig. 6. (Color online) (a) Eu-doped ZnO–Li_3NbO_4 concentration-dependent PL intensity ratio of $^5D_0$-$^7F_1$(R)/$^5D_0$-$^7F_2$(O). (b) Emission spectra of ZnO–Li_3NbO_4:$x$$Eu^{3+}$ (x = 1, 3, 5, 7, and 9%).

where a is the absorption coefficient, C is a constant, hv is the photon energy, and E_g is the energy band gap. The E_g of Eu^{3+}-doped ZnO–Li_3NbO_4 was 3.13–3.24 eV. This result was similar to previously reported results.[11,14]

Figure 6(a) shows the PL intensity–wavelength image of Eu^{3+} ions, which shows an excitation band at λ_{ex} = 466 nm ($^7F_0 \rightarrow {}^5D_2$). The excitation and emission intensities of the 4f inner layer of the orbital transition of Eu^{3+}-doped ZnO–Li_3NbO_4 predominantly showed the characteristic absorption peaks.[11] In the image, the first emission peak and the highest emission peak, which is classified as orange light, appear at λ_{em} = 595 nm ($^5D_0 \rightarrow {}^7F_1$) and λ_{em}= 615 nm ($^5D_0 \rightarrow {}^7F_2$), respectively.

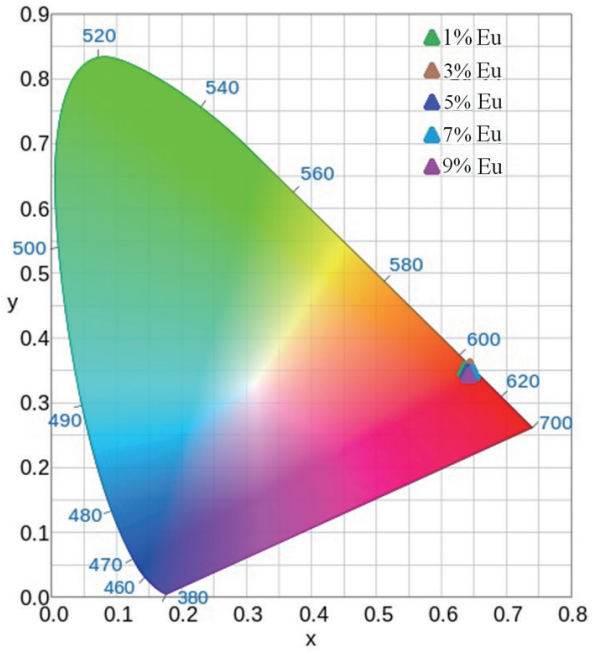


Fig. 7. (Color online) CIE color coordinate diagram of ZnO–Li_3NbO_4:xEu^{3+} (x = 1, 3, 5, 7, and 9%).

Figure 6(b) shows that the luminous intensity was observed to be the highest at 5% Eu^{3+} and began to decrease at 7% Eu^{3+}. This was caused by the transfer of energy, during which the activator ion concentration saturated and reached its maximum simultaneously.[11] This revealed that the concentration of crystal defects attributed to the luminous intensity decreased during the transfer of energy. The concentration-dependent intensity ratios of $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$(R/O) for 1, 3, 5, 7, and 9% Eu^{3+}-doped ZnO–Li_3NbO_4 were 2.04, 0.92, 2.21, 0.94, and 2.12, respectively. When the concentration of the Eu^{3+} dopant was increased to 5% to form Eu^{3+}-doped ZnO–Li_3NbO_4, the intensity ratio (R/O) became maximum.

Figure 7 shows CIE color coordinates of ZnO–Li_3NbO_4 with 1 to 9 mol% Eu^{3+} doping concentrations. The CIE chromaticity coordinates show the shifted area at about x = 0.65 and y = 0.35, which was located at an orange-red light area. Such coordinates were not clearly affected by the different Eu^{3+} doping concentrations.

4. Conclusions

In this study, Eu^{3+}-doped ZnO–Li_3NbO_4 was successfully synthesized. XRD analysis showed that the ZnO–Li_3NbO_4 structure gradually formed at 400 °C and the highest crystallinity was obtained at 900 °C. When 5% Eu^{3+} was doped into the ZnO–Li_3NbO_4 structure, the highest emission intensity of $^5D_0 \rightarrow {}^7F_1$ (466 nm) was obtained. When the CIE color coordinates of Eu^{3+}:ZnO–Li_3NbO_4 (about x = 0.65 and y = 0.35) were obtained, an orange-red sample was similarly observed at 5% Eu^{3+}. These results will be useful in the field of biological and optical detection.

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