Photoluminescent characterization of KNbO$_3$:Eu$^{3+}$

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Abstract

In this study, the photoluminescence (PL) spectra of europium-doped potassium niobate (KNbO$_3$) crystallites prepared by a vibrating milled solid-state reaction method were studied. X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical spectral analysis (luminescence excitation, emission spectra and time-resolved spectra) were used to characterize the KNbO$_3$:Eu$^{3+}$ powders. The results of the XRD revealed that the powders remained as a single orthorhombic structure at doping concentrations below 3 mol%. A second phase of EuNbO$_4$ begins to appear at 5 mol%. The $^5D_0$–$^7F_1$ (593 nm) and $^5D_0$–$^7F_2$ (614 nm) emission characteristics of Eu$^{3+}$ appear at a quenching concentration of above 3 mol%. The Commission Internationale d’Eclairage (CIE) chromaticity coordinates of a Eu:KNbO$_3$ host excited at $\lambda_{ex} = 400$ nm and $\lambda_{ex} = 466$ nm wavelengths, both presented a red-shift when increasing the Eu$^{3+}$ ion doping. The lifetime of the Eu$^{3+}$ ion decreased as the doping concentration was increased from 1 to 7 mol%.

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1. Introduction

Rare-earth (RE)-doped materials have been of great scientific interest in photonic devices and next-generation flat-panel displays. The luminescence characteristic of rare-earth -doped materials is slightly affected by both the host material and temperature. This feature can be used to tune the emission spectra for specific applications. Thus, it is important for the systematic research of rare-earth ions doped in different kinds of host materials having good mechanical, thermal, electrical and electro-optical properties [1,2].

Recently many Eu$^{3+}$-doped materials have been extensively studied because of the intra-4f-shell transitions that occurs from the excited level down to the lower levels: $^5D_0 \rightarrow ^7F_j$ ($j = 1, 2, 3, 4$) for Eu$^{3+}$ions [3,4]. The emission intensity was dominated by wavelength peaks at around 610–630 nm. This can be attributed to the transition of $^5D_0 \rightarrow ^7F_2$ which showed bright red luminescence and laser action in a variety of different glasses and single crystals [5,6].

Potassium niobate (KNbO$_3$) is a useful candidate for ferroelectric materials with excellent electro-optic and nonlinear optical coefficients which have attracted a great amount of interest for applications in optical waveguides, frequency doublers and holographic storage systems [7,8]. Therefore, KNbO$_3$ is a good candidate for RE doped host materials. Wen et al. [9,10] studied the Stokes photoluminescence (PL) spectra of erbium doped KNbO$_3$. They found that the PL spectra were significantly affected by the dopant concentration. However, to our knowledge, europium-doped KNbO$_3$ has not been thoroughly investigated yet [11,12], which was the motivation for this research.

In this study, different Eu$^{3+}$-doped KNbO$_3$ were achieved using a vibrating milled solid-state reaction method. The effect of Eu$^{3+}$ doped KNbO$_3$ was carefully examined by X-ray powder diffraction using a Cu K$_\alpha$ radiation (Rigaku Dmax-33 X-ray diffractometer).
with a source power of 30 kV 20 mA to identify the possible phases. The surface morphology was examined by high-resolution scanning electron microscopy (HR-SEM, S4200, Hitachi). The PL spectra was recorded at room temperature with a Jobin Yvon HR-320 monochromator and an Avantes USB-2000 detector by scanning the wavelength region from 200 to 1000 nm under an excitation of UV rays using a Perkin-Elmer 300 W Xenon lamp.

3. Results and discussion

Fig. 1 shows the XRD patterns of different concentrations of Eu$^{3+}$-doped KNbO$_3$. The peaks of the Eu$^{3+}$:KNbO$_3$ ceramics pattern matched very well with the JCPDS: 32–0822 data. All samples belonged to the orthorhombic structure because of the split of the diffraction peaks, (2 2 0) and (0 0 2) [15]. According to previous researchers [16,17] who studied KNbO$_3$ crystal in detail the rhombohedral phase transforms to the orthorhombic, then to the tetragonal and finally to the cubic phase at 263, 498 and 708 K, respectively.

The Eu$^{3+}$:KNbO$_3$ powders did not change their orthorhombic crystal structure when increasing the doping concentrations from 0 to 7 mol%. However, as the europium concentration was increased beyond a certain limit, the redundant europium ions nullified the precipitation effect. The peak appeared at the diffraction angle $2\theta$ of 28.10 and $2\theta$ of 29.72 and showed the existence of a small amount of second phase crystallization at Eu$^{3+}$ doped concentrations over 5 mol% and sintered at a temperature of 1020°C. The second phase peaks were identified to be the EuNbO$_4$ phase (JCPDS file: 22–1099). How the second phase influenced the emission properties will be discussed later in this paper.

![Fig. 1. XRD patterns of KNbO$_3$ at different Eu$^{3+}$ concentrations and sintered at 1020°C.](image)

Fig. 2(a)–(d) are the SEM images and show the surface microstructures of the four Eu$^{3+}$:KNbO$_3$ compositions. The KNbO$_3$ powders with a Eu$^{3+}$ doping concentration in the range of 1–7 mol% do not have any obvious differences in morphol-

![Fig. 2. Scanning electron micrographs of KNbO$_3$ at different Eu$^{3+}$ concentrations: (a) 1 mol%, (b) 3 mol%, (c) 5 mol% and (d) 7 mol%.](image)
The particle diameter of Eu$^{3+}$:KNbO$_3$ is about 0.3–0.5 μm. The particle diameter of pure KNbO$_3$ is 0.6 μm. The dopant reduced the size of the microcrystallites as compared to pure KNbO$_3$. In pure as-grown potassium niobate crystals, a rectangular crystalline growth was found and the growth appears to be the layer type [18]. This indicates that a dopant of Eu$^{3+}$ ions in KNbO$_3$ does not affect the crystal morphology at the same thermal treatment temperature. The nucleation density of the microcrystallites increased in Eu$^{3+}$:KNbO$_3$ powders compared with pure KNbO$_3$ powders. Nucleation and growth rates were influenced by the presence of impurities, lowering the potential barrier for the formation of nuclei and slowing the growth velocities, which were likely responsible for decrease in the grain size.

The normalized excitation spectra of the KNbO$_3$:Eu$^{3+}$ samples are shown in Fig. 3. The charge transfer band plays an important role in its luminescence. The adsorbed spectra shows, when the wavelength ranged from 370 to 480 nm that the sharp peaks originated from the transitions with the f-configuration from $^7F_0$ to the excitation states [19]. The excitation wavelength $\lambda_{ex}$ is 593 nm. While the broadband around 320 nm may attribute to the transition from the valence band, which is mainly the O 2p orbitals, to the conduction band, which is composed of mainly the d orbitals of the transition metals. The transition that occurs at about 320 nm can be attributed to a charge transfer from the O$^{2-}$ ligands to the empty 4d orbitals of the Nb (V) ions [20].

The charge transfer transition of O$^{2-}$–Eu$^{3+}$, which normally appears at about 250 nm, is not present in these materials. For the solid KNbO$_3$ with doped Eu$^{3+}$ concentrations, it can be seen that a maximum charge transfer occurred for the sample with a concentration of $C_{Eu}=5\%$, but for the sample with a concentration of $C_{Eu}=7\%$, the excitation spectrum consisted of only a sharp line Eu excitation and no charge transfer band could be detected, actually similar phenomenon has been observed for another solid K$_{13}$Eu(SiW$_{11}$O$_{39}$)$_2$ [21]. At the $^7F_0$–$^5L_6$ transitions the sample doped with an Eu concentration of 7% under higher intensity excitation position related to the $^7F_0$–$^5D_2$ transitions shifted to a higher energy (shorter wavelength). This phenomenon may be explained as the second phase EuNbO$_4$ aggregate in the microstructure.

The Eu$^{3+}$:KNbO$_3$ exhibited orange and red emission excited at $\lambda_{ex} = 400$ nm and $\lambda_{ex} = 466$ nm and are shown in Fig. 4(a) and (b). The emission spectra were dominated by the two transitions of $^5D_0$–$^7F_1$ (593 nm) and $^5D_0$–$^7F_2$ (614 nm). It is well known that $^5D_0$–$^7F_1$ is a magnetic dipole transition in nature and is also independent of the crystallographic site of the Eu$^{3+}$ ions. $^5D_0$–$^7F_2$ is an electric dipole transition implying that Eu$^{3+}$ ions occupy the noncentrosymmetric sites. However, increasing the Eu$^{3+}$ ions made the ions distribute throughout the noncentrosymmetric sites. The crystallizing KNbO$_3$ system in a slightly distorted perovskite structure (Bmm2) [16], with an orthorhombic unit cell of Nb ions of 0.69 Å, will be substituted by the Eu$^{3+}$ ions of 1.13 Å, occupying the octahedral sites. This is because of an obvious luminescent effect during the magnetic-dipole transition. When the Eu concentration reached 5% and the second phase of the EuNbO$_4$ started to appear the emission intensity largely decreased at the centrosymmetric sites. Therefore, the
presence of EuNbO$_4$ showed strong emission intensity at the noncentrosymmetric sites.

The KNbO$_3$ doped at 3% Eu reached a saturated photoluminescence intensity at the $^5$D$_0$–$^7$F$_1$ position. The sample with $C_{\text{Eu}}$ = 5% caused a weak photoluminescence intensity at the $^5$D$_0$–$^7$F$_1$ and $^5$D$_0$–$^7$F$_2$ positions. Two reasons can explain this phenomena: (1) an increased defect density in the sample with a higher Eu concentration and (2) the concentration quenching effect [22,23]. However, increasing doped concentration up to $C_{\text{Eu}}$ = 7% not only led to an increase in the peak intensity but also had a shift of the PL peak wavelength from 614 to 612 nm at the $^5$D$_0$–$^7$F$_2$ spectral site. For these observations, the main possible reasons can be attributed to the crystal field results. As the higher Eu$^{3+}$ dopants were incorporated into the pure KNbO$_3$ it caused the second phase to precipitate, so the change of coulomb attraction force the activator (Eu$^{3+}$) to experience different crystal field, and lead to the red-shift or blue-shift on the emission spectra [24]. The second phase EuNbO$_4$ aggregate would increase the Eu atoms occupying the noncentrosymmetric sites due to the forced electric dipole transition $^5$D$_0$ → $^7$F$_2$ becoming hypersensitive [25] and its emission intensity extensively increasing. In this study, a proportion of Eu$^{3+}$ ions may stack on the sites out side of the host. The emission behavior of Eu$^{3+}$ ions were effected by the crystal field, so that more than one emission mechanism will be introduced in the biphasic crystallites. Generally, the decaying behavior of emission could be used to identify that the emission’s mechanisms were employed in the luminescence process.

Fig. 5 shows the concentration-dependent PL intensity ratio of Eu-doped KNbO$_3$ to be $^5$D$_0$ → $^7$F$_2$/$^5$D$_0$ → $^7$F$_1$ (R/O). It can be seen that the intensity ratio (R/O) increased as the Eu$^{3+}$ dopants were increased. The Commission Internationale d’Eclairage (CIE) chromaticity coordinates of KNbO$_3$ polycrystalline at different concentration of Eu$^{3+}$ doping excited at $\lambda_{\text{ex}}$ = 400 nm and $\lambda_{\text{ex}}$ = 466 nm, are listed in Table 1. At 400 nm blue ray excitation, the color of the emission light, shifts from an orangish red to a pinkish red as the doping concentrations were increased. At a 1 mol% doping level, the CIE color coordinate were $x$ = 0.587 and $y$ = 0.403; for a 7 mol% doping level, the CIE color coordinate were $x$ = 0.592 and $y$ = 0.400. In addition, the colors of the emission light at a 466 nm green ray excitation were similar to those at a 400 nm blue ray excitation. From the data in Table 1, the CIE color coordinate for a 1 mol% doping level to a 7 mol% doping level shifts from $x$ = 0.570 and $y$ = 0.422 to $x$ = 0.594 and $y$ = 0.400. Which represents a red-shift as the Eu$^{3+}$ ion doping levels were increased.

The room temperature decay time of the emission from the $^5$D$_0$ state of Eu$^{3+}$ in KNbO$_3$ at different doping concentration is listed in Fig. 6. Effective time-resolved emission spectra were carried out at an excitation of 593 nm. The lifetime $\tau$ is described as $(\gamma_r + \gamma_{nr})^{-1}$, where $\gamma_r$ and $\gamma_{nr}$ are the radiative rate and the non-radiative rate (by quenching), respectively. It can be seen that the higher the doping concentration, the shorter the lifetime. The lifetime of the Eu$^{3+}$ $^5$D$_0$ level at the C$_{3v}$ site decreased from 1.18 ms when $C_{\text{Eu}}$ = 1% to 0.62 ms when $C_{\text{Eu}}$ = 7%. This

### Table 1

<table>
<thead>
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<th>[Eu]%</th>
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![Fig. 5. Eu-doped KNbO$_3$ concentration-dependent PL intensity ratio of $^5$D$_0$–$^7$F$_2$/$^5$D$_0$–$^7$F$_1$ (R/O).](image1)

![Fig. 6. Concentration-dependent Eu-doped KNbO$_3$ powders luminescence decay curves of sintered at 1020 °C.](image2)
behavior may have been caused by the variable nature of the surrounding medium between the second phase and the crystalline structure. The decrease in the lifetime when the doped concentration was increased can be attributed to the non-radiative relaxation caused by the surface defects that act as a quenching center. When the doped concentration was increased, the sample had more and more quenching centers and the non-radiative rate increased, which caused the lifetime to be shortened.

Ozawa et al. [26] studied the lifetime of Eu$^{3+}$ at different sites in cubic Y$_2$O$_3$. They found that Eu$^{3+}$ ions at the C2 and the S6 sites were responsible for a longer lifetime of about 1 ms and >4 ms, respectively. In this study, the decay of $^5$D$_0$ level at 1% and 3% Eu$^{3+}$ doped onto orthorhombic KNbO$_3$ was quite similar and this was due to the Eu$^{3+}$ ions being well defined at the lattice site and hence the mentioned lifetime. The sample with $C_{Eu} = 5\%$ had reached a concentration quenching effect and caused a shorter lifetime. Therefore, when the Eu concentration was increased to 7%, the time resolved spectra showed a unsmooth exponential curve with smaller peaks and shorter lifetimes. Due to the concentration quenching effect, the second phase of the EuNbO$_4$ and other cation ions were exited at higher-doped concentrations. The quenching centers of the host materials vibrated due to these impurities and resulted in the decrease in the Eu$^{3+}$ lifetime. It was also observed that the coexistence of the orthorhombic KNbO$_3$ and the second phase of the EuNbO$_4$ effected the decay of the curve morphology.

4. Conclusions

In this study, the Eu$^{3+}$-doped KNbO$_3$ had been successfully synthesized using a solid-state reaction method. The following results were obtained:

(1) When the single orthorhombic KNbO$_3$ crystalline structures doping concentration was increased from 0 to 3 mol% the crystalline structures remained as a single orthorhombic structure. When the sample’s $C_{Eu}$ was no less than 5%, the EuNbO$_4$ phase started to appear.

(2) When the amount of europium ions doped at 3% into the KNbO$_3$ crystalline structure, the best emission intensity of $^5$D$_{0}$-$^7$F$_{1}$ (593 nm) was found at the centrosymmetric sites.

(3) When the CIE color coordinate of the Eu:KNbO$_3$ was excited at $\lambda_{ex} = 400$ nm and $\lambda_{ex} = 466$ nm, the red-shift occurred when the Eu$^{3+}$ ions were increased.

(4) When the doping concentration was increased, the lifetime became shorter.

(5) It was observed that the coexistence of the orthorhombic KNbO$_3$ and the second phase of the EuNbO$_4$ effected the decay of the curve morphology.

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