

Spectroscopic properties and thermally stable orange-red luminescence of Sm:Zr:LiNbO₃ and Sm:Hf:LiNbO₃ for white LED applications

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ARTICLE INFO

Keywords:

LiNbO₃
Spectroscopic properties
Orange-red luminescence
Luminescent thermal stability

ABSTRACT

LiNbO₃ crystals activated by Sm³⁺ and co-doped with Zr⁴⁺ (Sm:Zr:LN) or Hf⁴⁺ (Sm:Hf:LN) were prepared by the Czochralski method. Detailed investigation on spectroscopic properties was conducted on the frame of Judd-Ofelt (J-O) theory. The J-O intensity parameters Ω_i ($i = 2, 4, 6$), fluorescence branching ratios and radiative lifetime of excited level ⁴G_{5/2} were determined. Furthermore, the thermal stability of the strong orange-red emissions obtained under near-UV excitation in both crystals was evaluated. As high as 100% and 97% of integrated intensities at room temperature in Sm:Zr:LN and Sm:Hf:LN respectively were retained at 423 K, demonstrating the suppressed thermal attenuation. The temperature sensing performance based on fluorescence intensity ratio strategy was degraded at higher temperatures with relatively low sensitivities, while the shift of CIE chromaticity coordinates of Sm:Zr:LN and Sm:Hf:LN in the orange-red region was insignificant, demonstrating the color constancy with increasing temperature. With the efficient and thermally stable orange-red luminescence, Sm:Zr:LN and Sm:Hf:LN could serve as promising candidate materials for near-UV excited white light-emitting diodes.

1. Introduction

White light-emitting diodes (WLEDs) [1], considered to be a new-generation solid-state light source, have received wide attention over decades owing to the significant advantages of low energy consumption, long durability, environmental friendliness and so on. Commonly, commercially available WLEDs are realized with blue GaN-LEDs coated with Ce³⁺:Y₃Al₅O₁₂ yellow phosphor [2]. However, in spite of the high luminescence efficiency and low preparation cost, the mainstream WLEDs suffer from a low color rendering index (CRI) and high correlated color temperature (CCT) due to lack of red spectral component. Alternatively, a scheme for fabrication of WLEDs via assembling green-, blue- and red-emitting phosphors on upper part of near-UV InGaN (350–420 nm) LED chip was proposed [3,4]. At the same time, in order to further improve the optical performance of WLEDs, great effort has been devoted to exploration for near-UV excited red

emitting phosphors with high luminescence efficiency.

In addition to Eu³⁺ which has been embedded in various crystals [5, 6] for red luminescence, Sm³⁺ is recognized to be an alternative activator with efficient orange-red emission originating from level ⁴G_{5/2} and well-matched absorption band in near-UV region. A sequence of Sm³⁺ doped phosphors for improved WLEDs has been reported. Notably, higher thermal stability of orange-red emission of Sm³⁺ compared to that of red emission of Eu³⁺ at higher temperatures was found [7], which is of practical significance against the thermally deteriorating of optical performance under high-power excitation. Besides, temperature sensing, which is to some extent opposite of thermal stability, could also be realized in Sm³⁺ doped phosphors based on the temperature dependent fluorescence intensity ratio (FIR) associated with transitions ⁴G_{5/2} → ⁶H_{5/2}/⁴G_{5/2} → ⁶H_{7/2} or ⁴G_{5/2} → ⁶H_{5/2}/⁴G_{5/2} → ⁶H_{9/2} [8]. Since the heating effect under near-UV excitation is inevitable, deteriorating temperature sensing, restraining thermal attenuation and achieving

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<https://doi.org/10.1016/j.ceramint.2020.09.027>

Received 4 August 2020; Received in revised form 2 September 2020; Accepted 3 September 2020

Available online 5 September 2020

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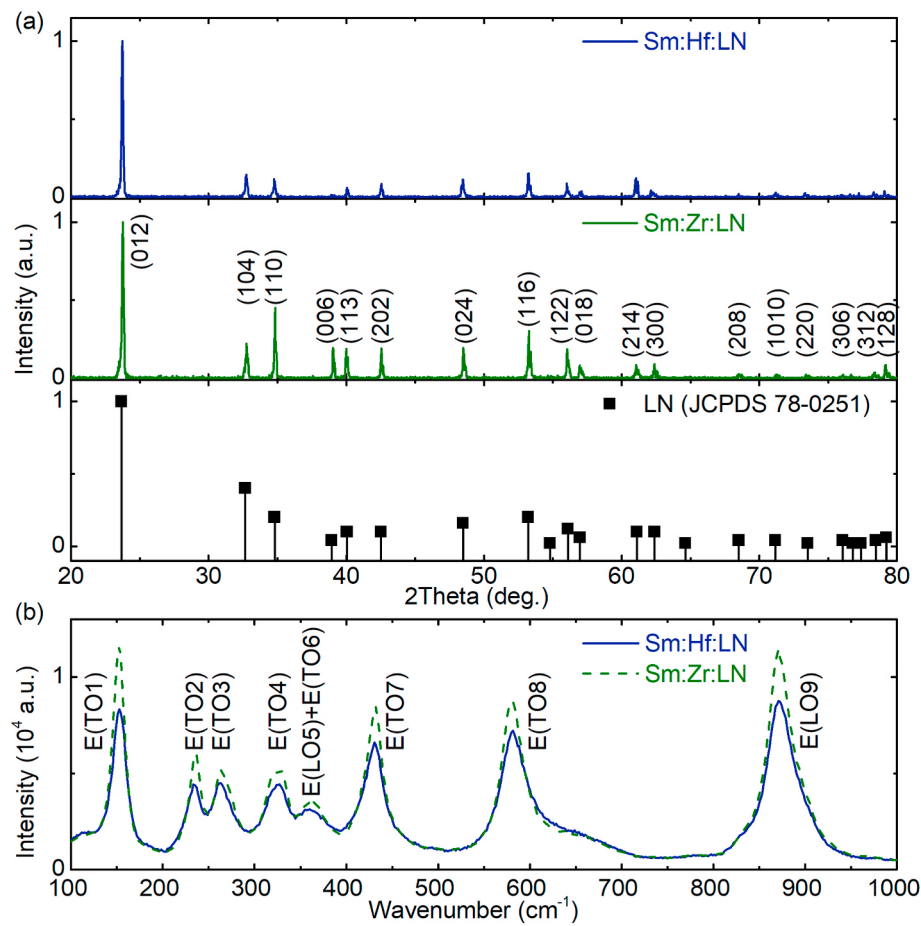


Fig. 1. (a) The X-ray power diffraction patterns of congruent LN (JCPDS 78-0251), Sm:Zr:LN and Sm:Hf:LN. (b) The Raman spectra of Sm:Zr:LN and Sm:Hf:LN.

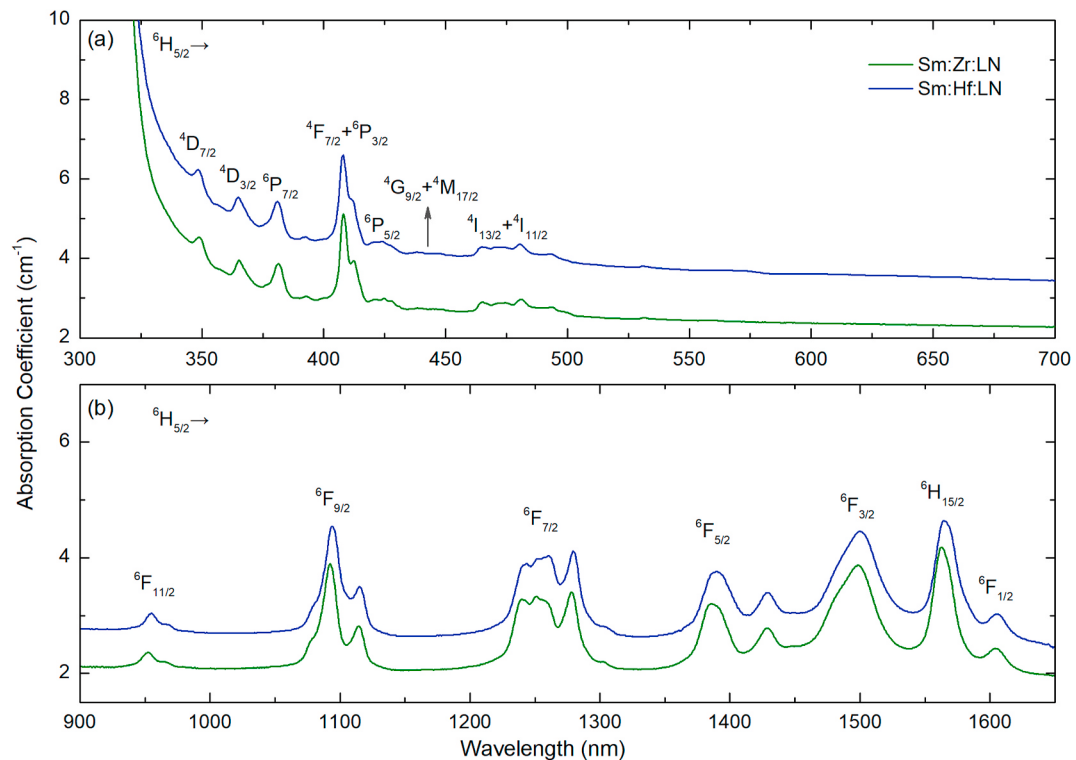


Fig. 2. The transmission absorption spectra of Sm:Zr:LN and Sm:Hf:LN crystals recorded at room temperature in (a) ultraviolet–visible and (b) near-infrared regions.

Table 1

Experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths, J-O parameters (Ω_2) and root mean square deviation (Δf_{rms}) of Sm:Zr:LN and Sm:Hf:LN.

Transition $^6\text{H}_{5/2} \rightarrow$	Energy (cm^{-1})	Oscillator strengths ($\times 10^{-6}$)			
		Sm:Zr:LN		Sm:Hf:LN	
		f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^4\text{D}_{3/2}$	27,322	0.52	0.91	1.162	0.893
$^6\text{P}_{7/2}$	26,247	0.96	1.32	1.895	1.413
$^4\text{F}_{7/2}, ^6\text{P}_{3/2}$	24,450	5.42	5.41	5.324	5.323
$^4\text{I}_{13/2}, ^4\text{I}_{11/2}$	21,164	2.16	3.05	3.035	3.195
$^6\text{F}_{11/2}$	10,493	0.38	0.34	0.379	0.377
$^6\text{F}_{9/2}$	9141	2.25	2.24	2.384	2.377
$^6\text{F}_{7/2}$	7962	2.76	3.71	2.983	3.831
$^6\text{F}_{5/2}, ^6\text{F}_{3/2}, ^6\text{F}_{1/2}, ^6\text{H}_{15/2}$	6680	2.93	2.93	3.019	2.802
J-O parameters (10^{-20} cm^2)		$\Omega_2 = 2.92$		$\Omega_2 = 2.65$	
		$\Omega_4 = 2.98$		$\Omega_4 = 2.93$	
		$\Omega_6 = 1.45$		$\Omega_6 = 1.55$	
root mean square deviation		$\Delta f_{\text{rms}} = 0.53$		$\Delta f_{\text{rms}} = 0.40$	

Table 2

Radiative transition probability A_r , fluorescence branching ratio β and radiative lifetime τ_r of Sm:Zr:LN and Sm:Hf:LN.

Transition $^4\text{G}_{5/2} \rightarrow$	λ_{em} (nm)	Sm:Zr:LN		Sm:Hf:LN	
		A_r (s^{-1})	β (%)	A_r (s^{-1})	β (%)
$^6\text{H}_{5/2}$	568	21.46	3.776	20.75	3.737
$^6\text{H}_{7/2}$	610	221.42	38.960	223.75	40.293
$^6\text{H}_{9/2}$	651	261.42	45.991	246.97	44.474
$^6\text{H}_{11/2}$	717	64.02	11.265	63.84	11.496
ΣA_r (s^{-1})		568.32		555.31	
τ_r (μs)		1759.57		1800.80	

stable luminescent performance are essential when exploring Sm^{3+} doped orange-red phosphors.

Versatile perovskite LiNbO_3 (LN) has been studied extensively for applications in laser, fluorescent displaying, biological imaging and so on, thanks to the excellent electro-optic, piezoelectric and non-linear optical properties [9,10]. With the high chemical and thermal stability, LN could serve as a promising candidate host for orange-red phosphors. A detailed investigation on Sm^{3+} doped LN has been conducted by Dominiak-Dzik [11], describing the spectroscopic characteristics

related to 4f electrons. In our previous work [12], the effect of Sm^{3+} concentration on orange-red emission in Sm:LN has been revealed. The anti-photorefractive ions, including Mg^{2+} , Zn^{2+} , In^{3+} , Hf^{4+} and Zr^{4+} , are usually introduced into LN at above threshold concentrations to eliminate intrinsic defects stemming from common Li-deficiency and suppress photorefractive effect [13]. Meanwhile the change of surrounding environment at rare earth (RE) ions might have important influence on the spectral properties: Enhanced near-infrared emissions were achieved in Er^{3+} :LN by Zr^{4+} co-doping [14]. Higher quenching temperature related to red emissions was found in Pr^{3+} :LN after heavily doping with Mg^{2+} [15]. Quadrivalent Zr^{4+} and Hf^{4+} present relatively low threshold concentrations of 2 mol% and 4 mol%. Hence, it is of great interest to know the spectroscopic properties, luminescent thermal stability and potential application possibility in WLEDs of Sm:LN with Zr^{4+} or Hf^{4+} codoping, which to our knowledge has not been explored yet.

In this work, Zr^{4+} and Hf^{4+} dopants at threshold concentrations were introduced in Sm:LN. The spectroscopic properties of Sm:Zr:LN and Sm:Hf:LN were analyzed systematically on the frame of the Judd-Ofelt theory. A focus of concern was on the orange-red photoluminescence performance and the luminescent thermal stability, the latter of which was studied by investigating thermal attenuation behavior, temperature sensing properties and CIE chromaticity coordinates. With the results, Sm:Zr:LN and Sm:Hf:LN were assessed as orange-red emitting component in near-UV excited WLEDs.

2. Experimental

The Sm:Zr:LN and Sm:Hf:LN single crystals with fixed Sm^{3+} concentration of 1.0 mol% were grown along the c axis by the Czochralski method. The concentrations of Zr^{4+} and Hf^{4+} were intended to be the thresholds of 2.0 mol% and 4.0 mol%. The molar ratio Li/Nb in congruent melt was 0.946. The raw materials (Li_2CO_3 , Nb_2O_5 , Sm_2O_3 , ZrO_2 and HfO_2) of 4 N purity were mixed thoroughly and calcined at 1150°C to form polycrystalline powders firstly. The single crystals were grown at the optimum technical conditions of a rotating rate of 15 rpm and a pulling rate of 1.5 mm/h. The wafer samples were cut from the central part of the as-grown crystals and then polished at both sides for further optical tests.

The crystallization phase was identified using an X-ray diffractometer (D-MAX-2200 VPC). The scattering angle 2θ was tuned from 20° to

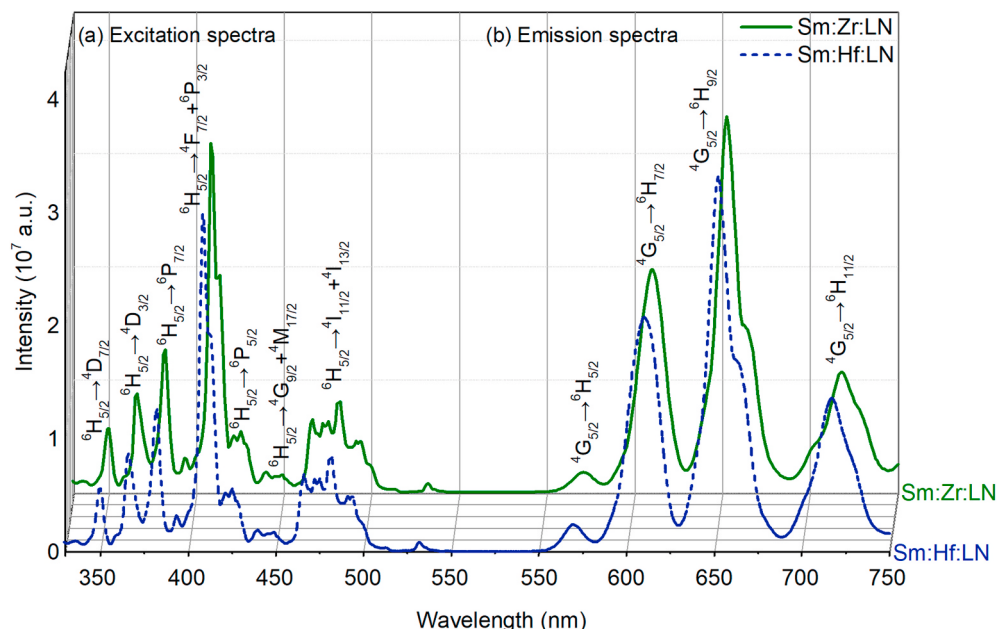


Fig. 3. The (a) excitation spectra monitored at 651 nm and (b) emission spectra under 409 nm excitation of Sm:Zr:LN and Sm:Hf:LN recorded at room temperature.

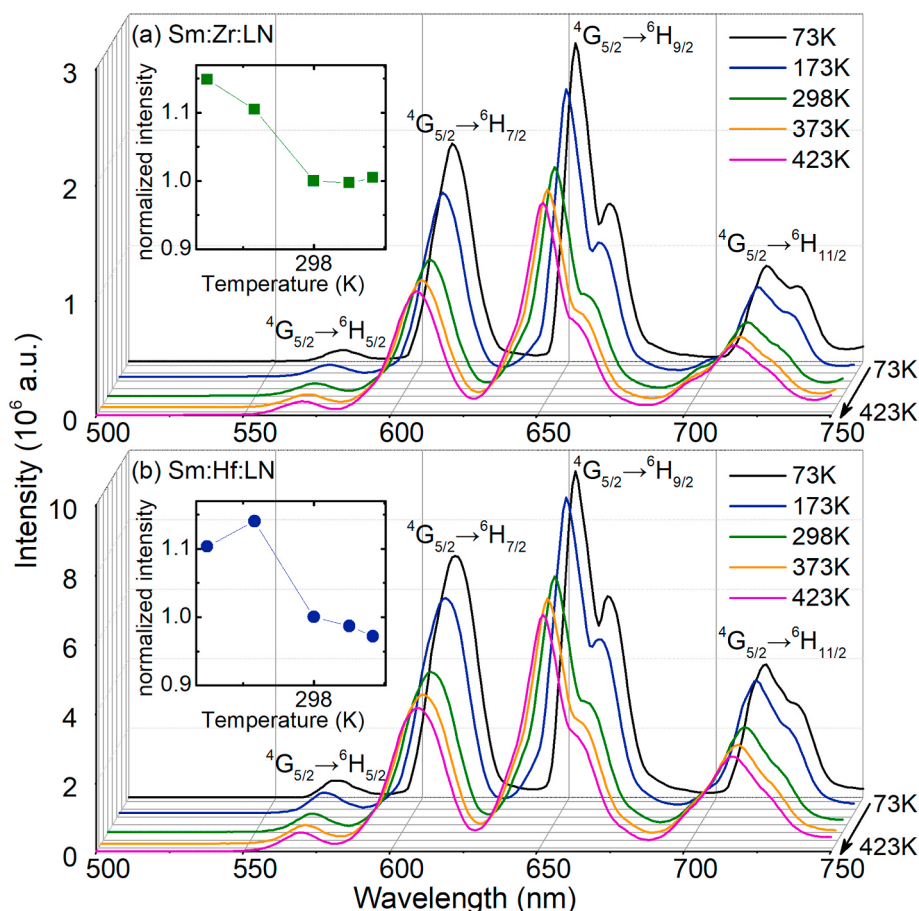


Fig. 4. The temperature dependent emission spectra of (a) Sm:Zr:LN and (b) Sm:Hf:LN excited at 409 nm. Insets showed the plots of integrated intensities associated with 4 visual emission bands as a function of temperature.

80° with a step of 0.02°. The Raman spectra in the range of 100–1000 cm^{-1} were recorded with an excitation wavelength of 514.5 nm using a Laser Micro-Raman Spectrometer (Renishaw inVia). The absorption spectra ranging from 300 nm to 1650 nm were recorded by a UV-VIS-NIR spectrophotometer (SHIMADZU, UV-3600) at room temperature. The fluorescence excitation and emission spectra were recorded using a photoluminescence spectrometer (Edinburgh, FLS920), which was equipped with a 450 mW Xe-lamp. Besides, a temperature controller (Advanced Research Systems) was combined to the photoluminescence spectrometer for the emission measurements at temperatures of 73, 173, 298, 373 and 423 K.

3. Results and discussion

3.1. Structure and phase analysis

The X-ray power diffraction patterns of Sm:Zr:LN and Sm:Hf:LN were shown in Fig. 1 (a), in contrast to the standard pattern of hexagonal congruent LN (JCPDS 78–0251) with space group $R3c$. All the diffraction peaks could be indexed to the known crystallographic planes of LN, while no new diffraction peaks were detected. The phase purity indicated that there were no noticeable changes in the lattice structure after impurity introduction. Dopants Sm^{3+} , Zr^{4+} and Hf^{4+} entered LN lattice by substituting Li^{+} and Nb^{5+} , instead of occupying the interstitial site within lattice. The Raman spectra of Sm:Zr:LN and Sm:Hf:LN were also measured at room temperature for characterizing crystal structure variation. As presented in Fig. 1 (b), the energy of the most energetic phonon was determined to be 870.99 cm^{-1} in both crystals. The well-defined Raman peaks marked with the corresponding vibrational

modes were attributed to LN structure and in good agreement with the data in previous study [16], indicating that there was only slight lattice distortion but no significant structure change in the LN crystals after codoping with the impurities of Sm^{3+} , Zr^{4+} and Hf^{4+} .

3.2. Spectroscopic properties and Judd-Ofelt analysis

The ultraviolet–visible (UV–Vis, 300–700 nm) and near-infrared (NIR, 900–1650 nm) transmission absorption spectra of Sm:Zr:LN and Sm:Hf:LN, containing features characteristics for Sm^{3+} impurity, were presented in Fig. 2. Numerous absorption peaks were detected, all of which originated from transitions from the ground level $^6\text{H}_{5/2}$ to excited levels of Sm^{3+} . The peaks centered at 349, 366, 381, 409, 423, 472, 953, 1094, 1256, 1391, 1501, 1565 and 1604 nm were ascribed to the excited levels $^4\text{D}_{7/2}$, $^4\text{D}_{3/2}$, $^6\text{P}_{7/2}$, $^4\text{F}_{7/2}$, $^6\text{P}_{3/2}$, $^6\text{P}_{5/2}$, $^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$, $^6\text{F}_{11/2}$, $^6\text{F}_{9/2}$, $^6\text{F}_{7/2}$, $^6\text{F}_{5/2}$, $^6\text{F}_{3/2}$, $^6\text{H}_{15/2}$ and $^6\text{F}_{1/2}$ respectively. Notably, the strong absorption band spanning wavelengths from 350 to 420 nm was suitable for optical pumping with commercial near-UV LED chip.

The effect of Zr^{4+} or Hf^{4+} codoping on spectroscopic properties of Sm:LN was investigated on the frame of Judd-Ofelt (J-O) theory. The J-O theory put forward by Judd [17] and Ofelt [18] in 1962 has been successfully applied to analyzing 4f–4f transitions in various rare earth doped crystals. By reference to the J-O theory computational process detailedly described in our previous study [12], the experimental and calculated oscillator strengths of Sm:Zr:LN and Sm:Hf:LN were calculated from the absorption spectra and presented in Table 1. The J-O intensity parameters Ω_t ($t = 2, 4, 6$) were derived using the doubly reduced matrix elements in Ref. [19] and also supplemented in Table 1. The trend of J-O parameter magnitude of Sm:Zr:LN and Sm:Hf:LN

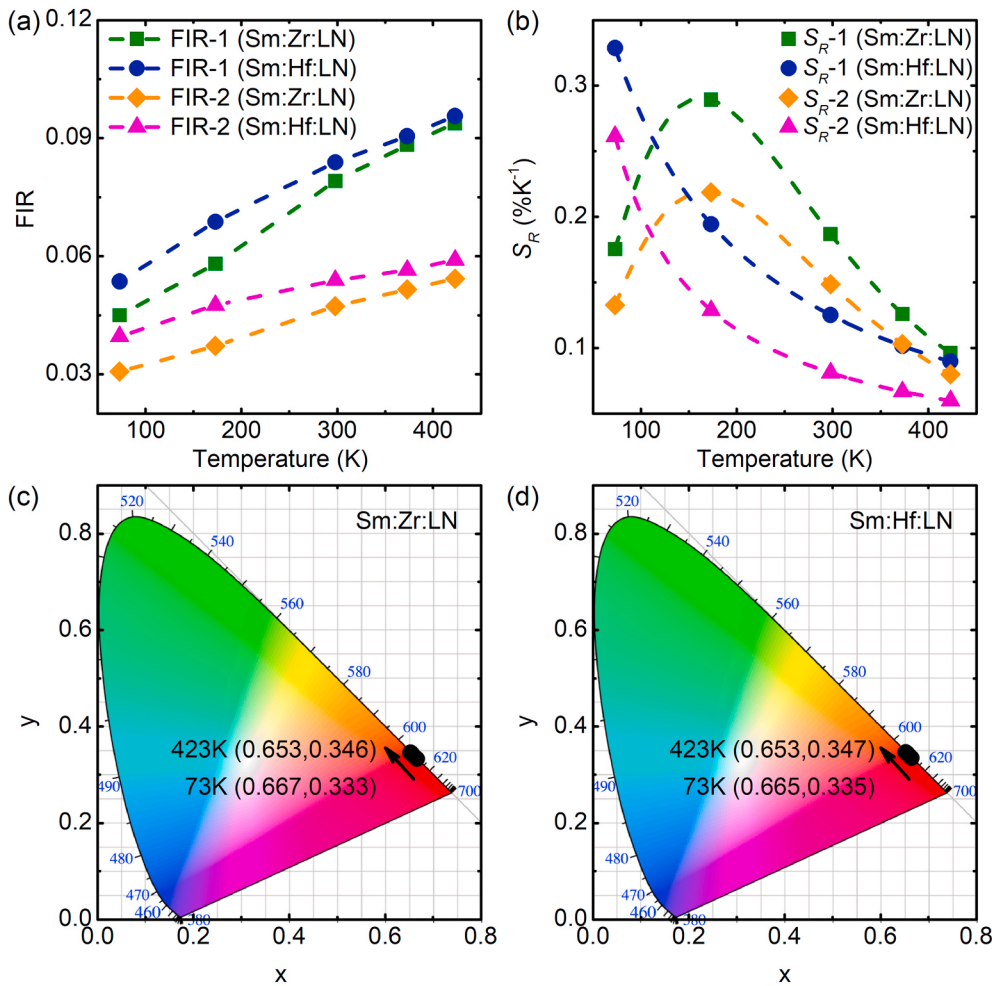


Fig. 5. (a) The temperature dependent FIR associated to transitions $^4G_{5/2} \rightarrow ^6H_{5/2}/^4G_{5/2} \rightarrow ^6H_{7/2}$ (FIR-1) and $^4G_{5/2} \rightarrow ^6H_{5/2}/^4G_{5/2} \rightarrow ^6H_{9/2}$ (FIR-2) of Sm:Zr:LN and Sm:Hf:LN under 409 nm excitation. (b) The corresponding relative sensitivity S_R . The CIE chromaticity coordinates of the orange-red emissions in (c) Sm:Zr:LN and (d) Sm:Hf:LN in the temperature range from 73 K to 423 K. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

remained $\Omega_4 > \Omega_2 > \Omega_6$, consistent with that of Sm (1 mol%):LN reported previously [12]. Ω_2 is sensitive to the covalent bonding between Sm^{3+} and ligand anions and structure asymmetry in the vicinity of Sm^{3+} [8]. The increase of Ω_2 in Sm:Zr:LN and Sm:Hf:LN compared with Sm:LN implied greater degree of covalency for Sm^{3+} -O²⁻ bond and higher asymmetry around Sm^{3+} after the substitution of anti-site Nb^{5+} with Zr^{4+} and Hf^{4+} . The estimated J-O parameters Ω_t were utilized to determine the important spectroscopic properties, including radiative transition probability A_r , fluorescence branching ratio β and radiative lifetime τ_r of the excited state. The results tabulated in Table 2 indicated that orange-red emissions originating from $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^6H_{9/2}$ with relatively long lifetime dominated in the visual region in Sm:Zr:LN and Sm:Hf:LN.

The experimental excitation spectra of Sm:Zr:LN and Sm:Hf:LN monitored at 651 nm were illustrated in Fig. 3 (a). There were sharp excitation peaks attributed to transitions from $^6H_{5/2}$ to $^4D_{3/2}$, $^6P_{7/2}$, $^4F_{7/2}$ and $^6P_{3/2}$ in both crystals. In spite of originating from forbidden $f-f$ transitions, the excitation peaks ranging from 350 to 420 nm were well compatible with the commercial near-UV LED chip, facilitating the application in near-UV excited devices. The strongest excitation peak centered at 409 nm was selected for the measurement of emission spectra, as illustrated in Fig. 3 (b). Sm:Zr:LN and Sm:Hf:LN exhibited similar emission characteristics, as derived via J-O analyzing. Strong orange-red light could be observed by naked eye, which was composed of green (568 nm), yellow (610 nm) and red (651 and 717 nm) emission bands, originating from transitions $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ respectively. Obvious splitting of 651 nm emission peaks owing to the crystal field effects [20] was observed.

With the dominant 610 and 651 nm emissions, Sm:Zr:LN and Sm:Hf:LN could make a significant contribution to increasing red spectral component in WLEDs for a higher CRI.

3.3. Thermal stability of orange-red emission

Low thermal attenuation of orange-red spectral component facilitated enhancing luminescence efficiency and CRI at high operating temperatures, and thus was important for practical applications in WLEDs. In general, high thermal stability of luminescence performance at 423 K ($\approx 150^\circ\text{C}$) was needed [21]. Hence, the temperature dependent emission spectra of Sm:Zr:LN and Sm:Hf:LN under 409 nm excitation at temperature ranging from 73 K to 423 K were recorded and presented in Fig. 4 (a) and (b) respectively. Gradual attenuation of integrated intensities associated with the 4 visual emission bands ($^4G_{5/2} \rightarrow ^4G_{5/2}$, $^4G_{7/2}$, $^4G_{9/2}$, $^4G_{11/2}$) was observed along when elevating the temperature, as depicted in the insets of Fig. 4. Based on the quantum mechanical single-configuration coordinate model [22,23], the thermal attenuation could be accounted for with the thermally accessible crossover between excited level $^4G_{5/2}$ and ground level $^6H_{5/2}$, which formed a channel for nonradiative relaxation. It should be noted that the orange-red emissions at 423 K retained 100% and 97% of the intensities at room temperature (298 K), significantly higher than the existing values ranging from 80% to 91% [21,24]. The strongly suppressed thermal attenuation confirmed the excellent thermal stability of orange-red emissions, demonstrating the potential application of Sm:Zr:LN and Sm:Hf:LN as orange-red component in WLEDs.

High color constancy at high temperatures was also important to

application in WLEDs, but adverse to application in temperature sensing. To evaluate the potential for optical thermometry, fluorescence intensity ratios (FIR) attributed to transitions ${}^4G_{5/2} \rightarrow {}^6H_{5/2}/{}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (FIR-1) and ${}^4G_{5/2} \rightarrow {}^6H_{5/2}/{}^4G_{5/2} \rightarrow {}^6H_{9/2}$ (FIR-2) of Sm:Zr:LN and Sm:Hf:LN were calculated and presented in Fig. 5 (a). Monotonous increase with increasing temperature was observed for all the FIRs, demonstrating that temperature sensing at temperatures ranging from 73 K to 423 K could be realized in both Sm:Zr:LN and Sm:Hf:LN via FIR measuring. The relative temperature sensitivity S_R , one of the most critical parameters to quantitatively characterize the temperature sensing performance, was determined and plotted in Fig. 5 (b) using the following formula:

$$S_R = \frac{1}{FIR} \frac{dFIR}{dT} \quad (1)$$

It was evident that the temperature sensing performance was degraded at higher temperatures with S_R below $0.1\%K^{-1}$ at 423 K. In contrast the thermal stability of colorimetric characteristics of orange-red emission was further enhanced with increasing temperature.

The CIE chromaticity diagrams, visually depicting the color variation with increasing temperature in Sm:Zr:LN and Sm:Hf:LN under 409 nm excitation were presented in Fig. 5 (c) and (d). The chromaticity co-ordinates of orange-red emissions in Sm:Zr:LN and Sm:Hf:LN shifted insignificantly, invariably located near the red standard value (0.670, 0.330) of National Television Standard Committee. The results directly confirmed color constancy and high thermal stability of orange-red emissions, with which Sm:Zr:LN and Sm:Hf:LN might be promising candidate materials for application in near-UV excited WLEDs.

4. Conclusions

In this work, Sm:Zr:LN and Sm:Hf:LN crystals were prepared by the Czochralski method. The phase purity of the as-grown crystals was analyzed based on the XRD patterns and Raman spectra. Detailed spectroscopic analysis on the frame of Judd-Ofelt theory was conducted. The J-O parameters of Sm:Zr:LN and Sm:Hf:LN were determined to be $\Omega_2 = 2.92 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.98 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 1.45 \times 10^{-20} \text{ cm}^2$, and $\Omega_2 = 2.65 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 2.93 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 1.55 \times 10^{-20} \text{ cm}^2$ respectively. Strong orange-red emissions under near-UV excitation were obtained in both crystals, consistent with the derived spectroscopic characteristics, including fluorescence branching ratios and radiative lifetimes. In spite of the thermal attenuation resulting from thermally nonradiative relaxation, as high as 100% and 97% of integrated emission intensities at room temperature were retained in Sm:Zr:LN and Sm:Hf:LN at 423 K, indicating the high thermal stability of orange-red emissions. Besides, the degraded temperature sensing performance based on FIR-1 (${}^4G_{5/2} \rightarrow {}^6H_{5/2}/{}^4G_{5/2} \rightarrow {}^6H_{7/2}$) and FIR-2 (${}^4G_{5/2} \rightarrow {}^6H_{5/2}/{}^4G_{5/2} \rightarrow {}^6H_{9/2}$) at higher temperatures with relatively low S_R and insignificantly shifting of chromaticity coordinates of orange-red emissions were demonstrated, indicating the color constancy with increasing temperature. With the results, Sm:Zr:LN and Sm:Hf:LN were proposed as promising candidate materials for application in near-UV excited WLEDs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by National Natural Science Foundation of China (11832019, 51802358), Science and Technology Planning Project

of Guangdong Province (2015B090927005), National Natural Science Foundation of Guangdong Province (2018A030313321, 2017A030310426), Fundamental Research Funds for the Central Universities (19lgpy273), and National Doctoral Program Fund (20130171130003).

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