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Optical thermometry using fluorescence intensities multi-ratios in $NaGdTiO_4:Yb^{3+}/Tm^{3+}$ phosphors

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The $NaGdTiO_4:Yb^{3+}/Tm^{3+}$ phosphor has been effectively synthesized by the traditional solid-state reaction method and its down-conversion and up-conversion luminescence properties were systematically studied. The results indicate that the electric dipole-dipole interaction is the main mechanism for the luminescence quenching. The fact that the ratios of the up-conversion intensities, i.e., I_{795nm}/I_{798nm}, I_{807nm}/I_{798nm}, and I_{812nm}/I_{798nm}, increase linearly with temperature (100 K–300 K) provides us a simple and accurate temperature measurement method. Multi-ratios can be more accurate than using only one ratio, allowing for self-referenced temperature determination. It's promising for $NaGdTiO_4$: Yb^{3+}/Tm^{3+} to be used for optical temperature sensors.

1. Introduction

Over the past few decades, temperature-dependent up-conversion luminescence of materials doped with lanthanide ions have attracted much attention, owing to their excellent properties such as non-contact temperature measurement, accurate and wide temperature range [1–4]. In particular, the non-contact optical thermometry via the fluorescence intensity ratio (FIR) is a potential temperature detection method in harsh environments. The FIR variation is attributed to the Boltzmann distribution, which can redistribute the populated electrons of thermally coupled energy levels at different temperatures [5]. Therefore, the FIR value is sensitive to the temperature and FIR technique can guarantee temperature measurement accuracy. To date, the $^1D_2 \to {}^3F_4/{}^3H_4 \to {}^3H_6$ [6], $^3F_{2,3} \to {}^3H_6/{}^3H_4 \to {}^3H_6$ [7], $^1D_2 \to {}^3F_4/{}^1G_4 \to {}^3H_6$ [8], $^1G_{4(a)} \to {}^3H_6/{}^1G_{4(a)} \to {}^3H_6$ [9–12], and $^3H_{4(1)} \to {}^3H_6/{}^3H_{4(2)} \to {}^3H_6$ [13,14] emission ratios of Tm^{3+} have been reported extensively to detect the temperature. Recently the intensity ratios of I_{788nm}/I_{808nm} in the $Bi_2O_3:Yb^{3+}/Tm^{3+}$ [13] and I_{797nm}/I_{807nm} [14] in the $NaNbO_3:Tm^{3+}$ were reported to exhibit a monotonic relationship with temperature for temperature sensing. The monotonic relationship can simplify the measurement process and improve data acquisition efficiency. Nevertheless, the only one ratio may be limited in practical applications. At this point, the work has reported the fluorescence intensity double ratios, which can broaden the temperature sensitivity range [15]. So it is necessary to study the fluorescence intensity multi-ratios to find some other new properties.

As is well known, the $NaGdTiO_4$ phosphors have been widely used as the host material owing to their superior physical, chemical stabilities, low cost and intense absorption band. Therefore, $NaGdTiO_4$: Yb^{3+}/Er^{3+} [1], $NaGdTiO_4$: $Yb^{3+}/Er^{3+}/Tm^{3+}$ [16,17], $NaGdTiO_4$: Sm^{3+} [18], $NaGdTiO_4$: Dy^{3+} [3] have been researched on the photoluminescence and temperature sensing properties.

Herein, $NaGdTiO_4$: Yb^{3+}/Tm^{3+} was effectively synthesized via traditional solid-state reaction method. The spectral splitting of energy level occurs in the infrared emission, which originates from transition $^3H_4 \to {}^3H_6$ of Tm^{3+} in $NaGdTiO_4$. The splitting of energy levels can be used as optical thermometry using their fluorescence intensities multi-ratios. The down-conversion, up-conversion and optical temperature sensing properties are systematically discussed. Results indicate that the fluorescence intensities multi-ratios exhibit monotonic relationship with temperature at the near infrared emission peaks, suggesting the material potential application in optical temperature sensors.

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2. Experimental

NaGdTiO$_4$: x%Yb^{3+}/y%Tm^{3+} (a) x = 16 (mol), y = 0.5, 1, 1.5, 2, 3, 5, 7, 9 (mol) and (b) x = 2, 4, 6, 10, 16, 18, 20 (mol), y = 1 (mol) were prepared using a conventional high temperature solid-state reaction method. Na$_2$CO$_3$, TiO$_2$, Gd$_2$O$_3$, Yb$_2$O$_3$, Tm$_2$O$_3$ were used as raw materials. Na$_2$CO$_3$ and TiO$_2$ were supplied by Tianjin Jiangtian Company and Mack Lin Company, respectively. Gd$_2$O$_3$(99.99%), Yb$_2$O$_3$(99.999%), Tm$_2$O$_3$(99.99%) were purchased from Beijing HWRK Chem Co., LTD. All raw materials were used as received without further refinement. After grinding, homogeneous mixtures were obtained and calcined at 1000 °C for 4 h in a high temperature resistance. A detailed preparation procedure could be found in Ref. [18].

X-ray diffraction (XRD) patterns were recorded with a Panalytical X-Pert Pro diffractometer using Cu Kα radiation with 40 mA and 40 kV. The microstructure were measured on JEM-2100 transmission electron microscopy (TEM). The morphology and the energy-dispersive X-ray spectroscopy (EDX) elemental mappings of the samples were observed with a scanning electron microscope (SEM) (JEOL JSM-7500F). Down-conversion and upconversion luminescent spectra measurements were carried out on Edinburgh Instruments FSP920 phosphorimeter using a 450W Xenon lamp as excitation source and an external 980 nm fiber laser as excitation source, respectively. Besides, the NaGdTiO$_4$: 16%Yb^{3+}/1%Tm^{3+} upconversion spectra in the range of 100 K–300 K was recorded on FLS 920P phosphorimeter using an external 980 nm fiber laser as excitation source.

3. Results and discussion

3.1. Phase identification

The structures of the samples were characterized by XRD. Fig. 1(a) shows the XRD patterns of NaGdTiO$_4$: 20%Yb^{3+}/1%Tm^{3+}, NaGdTiO$_4$: 16%Yb^{3+}/1%Tm^{3+}, NaGdTiO$_4$: 2%Yb^{3+}/1%Tm^{3+}, NaGdTiO$_4$: 16%Yb^{3+}/9%Tm^{3+}, NaGdTiO$_4$: 16%Yb^{3+}/3%Tm^{3+}, and NaGdTiO$_4$: 16%Yb^{3+}/0.5%Tm^{3+}, as representatives. It is found in the XRD results that the patterns are well identified with JCPDS standard card no. 86-0830 and there are no extraneous diffraction peaks emerging in these patterns, which means that the doping of the Tm^{3+}/Yb^{3+} ions do not affect the crystal phase of NaGdTiO$_4$.

Fig. 1(b) shows the SEM image of NaGdTiO$_4$ phosphors. It can be seen that the sample possesses schistose-like morphology, similar to previous report [19]. EDX elemental mappings of NaGdTiO$_4$ are displayed in Fig. 1(c)-(f). The elements of Na, Gd, Ti and O distribute homogeneously over the whole range of the sample. In this work, we choose a single small particle with size about 100 nm (Fig. 1(g)) and measure the high-resolution TEM (HRTEM) image (Fig. 1(h)). The crystal lattice, with an interplanar distance d value of 3.22 Å, is corresponding to the (211) crystal plane of NaGdTiO$_4$ (JCPDS No: 86-0830).

3.2. Down-conversion emission

Photoluminescence spectra in the visible region under 355 nm excitation of NaGdTiO$_4$: 16%Yb^{3+}/x%Tm^{3+} as a function of Tm^{3+} contents are shown in Fig. 2 and the integrated emission intensities

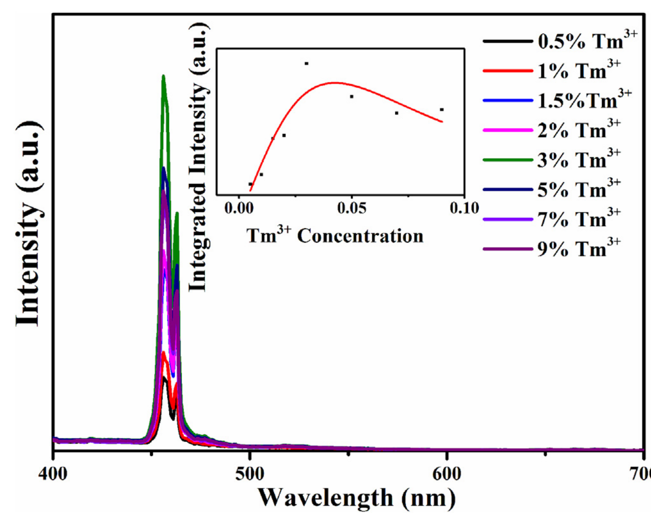

Fig. 2. Emission spectra of NaGdTiO$_4$:16%Yb^{3+}/y%Tm^{3+} (y = 0.5, 1, 1.5, 2, 3, 5, 7, 9) under 355 nm excitation. The inset is the dependence of integrated emission intensity on doping concentration of Tm^{3+}. The solid curve is the fitting result based on the Van Uitert's model.

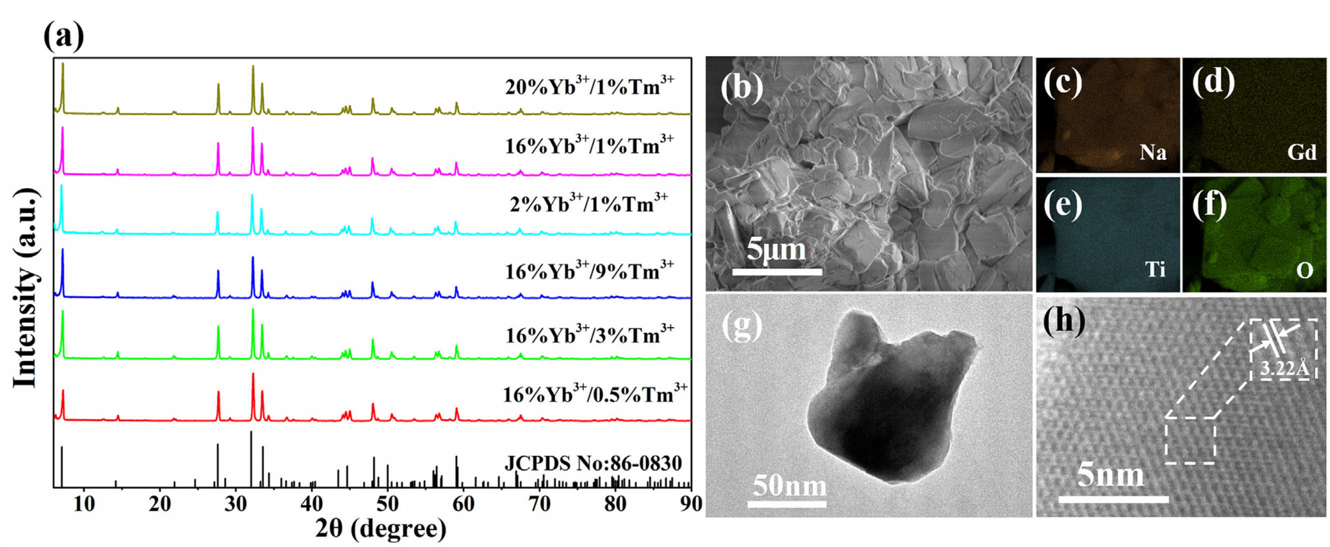

Fig. 1. (a) XRD patterns of NaGdTiO$_4$ phosphors doped with different ions and the reference data of JCPDS card No. 86-0830 for NaGdTiO$_4$. Characterizations of NaGdTiO$_4$ phosphors: (b) SEM image; (c)–(f) EDX elemental mappings; (g) TEM spectrum; (h) HRTEM image.