



Energy transfer from VO_4^{3-} group to Sm^{3+} ions in $\text{Ba}_3(\text{VO}_4)_2:3x\text{Sm}^{3+}$ microparticles: A bifunctional platform for simultaneous optical thermometer and safety sign

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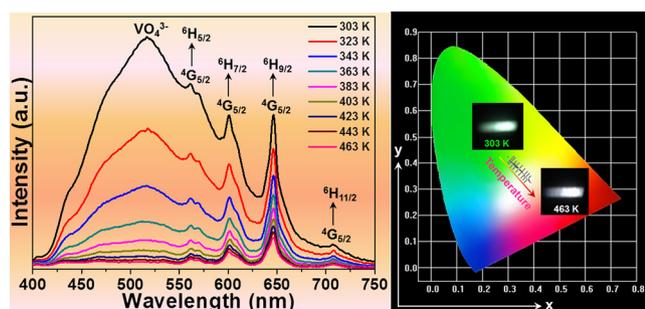


HIGHLIGHTS

- All the samples can be excited by NUV light and the optimal doping content was 4 mol%.
- The energy transfer efficiency from VO_4^{3-} group to Sm^{3+} ions reached up to 82.3% when $x = 0.2$.
- The FIR value of PL emission intensities of Sm^{3+} to VO_4^{3-} was dependent on the temperature.
- The maximum absolute and relative sensor sensitivities were 0.039 K^{-1} and $2.24\% \text{ K}^{-1}$, respectively.
- The emitting color relied on the temperature, which makes it suitable for safety sign.

GRAPHICAL ABSTRACT

Critic acid-assisted sol-gel synthesis of bifunctional $\text{Ba}_3(\text{VO}_4)_2:3x\text{Sm}^{3+}$ microparticles for non-contact optical temperature sensor and safety sign.



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ABSTRACT

The Sm^{3+} -doped $\text{Ba}_3(\text{VO}_4)_2$ microparticles were successfully synthesized via a simple sol-gel method. Both the recorded three-dimensional photoluminescence (PL) emission spectra and counter lines revealed that the near-ultraviolet light was a proper excitation lighting source for the studied samples. Under 352 nm of irradiation, the effect of Sm^{3+} ion concentration on the PL emission properties of the microparticles was investigated and the optimum doping concentration was demonstrated to be 4 mol%. Based on the diversity in the thermal quenching performance of VO_4^{3-} group and Sm^{3+} ions, a novel self-referencing non-invasion optical thermometer with high sensitivity and superior signal discriminability was designed. By taking the advantage of the temperature-dependent fluorescence intensity ratio between the VO_4^{3-} group and Sm^{3+} ions, the optical thermometric properties of the Sm^{3+} -doped $\text{Ba}_3(\text{VO}_4)_2$ microparticles in the temperature range of 303–463 K were analyzed. The maximum absolute and relative sensor sensitivities, which were hardly influenced by the PL emission intensity, were obtained to be 0.039 K^{-1} and $2.24\% \text{ K}^{-1}$, respectively. Furthermore, the emitting color of the resultant compounds was found to be significantly dependent on the external temperature. These results suggest that the Sm^{3+} -doped $\text{Ba}_3(\text{VO}_4)_2$ microparticles are a potential candidate for high-performance self-referencing optical thermometer and safety sign applications.

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1. Introduction

Over the last decades, great interest in optical thermometry based on rare-earth (RE) ions doped luminescent materials by utilizing the fluorescence intensity ratio (FIR) technique has been received since it cannot only circumvent the shortages of tradition contact thermometers (*i.e.*, low resolution and long response time) but also can be employed to monitor the temperature distribution of micro-systems, living cells, corrosive circumstances and fast moving objects [1–5]. In this technique, the temperature-dependent FIR value between the emission intensities arising from two thermally coupled levels of RE ions is the vital part to determine the optical thermometric performance of sensing materials. Up to date, lots of optical thermometers based on the temperature-triggered inverse electron population in thermal coupled levels of RE ions, such as Er^{3+} (${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$), Nd^{3+} (${}^4\text{F}_{3/2(1)}$, ${}^4\text{F}_{3/2(2)}$), Tm^{3+} (${}^3\text{F}_3$, ${}^1\text{G}_4$) and Eu^{3+} (${}^5\text{D}_0$, ${}^5\text{D}_1$), have been developed [6–9]. Wang *et al.* mentioned that the Er^{3+} -doped Y_2O_3 microtubes and $\text{NaYF}_4:\text{Nd}^{3+}@\text{NaYF}_4:\text{Yb}^{3+}$ core-shell nanoparticles can be used as optical temperature sensors by the FIR technique [10,11]. However, these kinds of temperature probes usually suffer from low accuracy due to the overlapped emissions induced by the small energy gap ($200\text{ cm}^{-1} < \Delta E < 2000\text{ cm}^{-1}$) between the thermally coupled levels as well as small relative sensor sensitivity (*i.e.*, $S_r = \Delta E/kT^2$) [12,13]. In order to avoid the above intrinsic limitations of the thermally coupled levels-based RE ions activated thermometric materials, a novel thermometry strategy should be proposed. Recently, the optical temperature sensors which rely on the phonon-assisted energy transfer between two activators along with their various thermal behaviors have been extensively investigated because of their superior temperature sensing ability. Zhang *et al.* designed a dual-emitting $\text{LaOBr}:\text{Ce}^{3+}/\text{Tb}^{3+}$ material system and used the efficient phonon-assisted energy transfer from Ce^{3+} to Tb^{3+} ions to achieve a sensor sensitivity of 0.014 K^{-1} at 473 K [14]. Moreover, Chen *et al.* proposed a $\text{NaGdF}_4:\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Ce}^{3+}@\text{NaYF}_4:\text{Yb}^{3+}/\text{Tm}^{3+}$ core-shell nanocrystal structure and its sensor sensitivity was found to be about 0.024 K^{-1} [15]. In addition, other combinations, such as $\text{Eu}^{3+}/\text{Tb}^{3+}$ -codoped metal-organic framework and $\text{Dy}^{3+}/\text{Cr}^{3+}$ -codoped $\text{Y}_3\text{Al}_5\text{O}_{12}$ phosphors, were also found to be potential candidates for self-referencing optical thermometry [16,17]. Despite these achievements, more efforts still should be made to further improve the sensor sensitivity to meet the requirement of practical applications.

As is known, choosing a proper luminescent host material, especially with low phonon energies, is very important to make the RE ions exhibit superior luminescent properties as well as allow their vivid applications. Compared with other inorganic materials, the vanadates which are regarded as an excellent luminescent host material for RE ions have been widely investigated for solid-state lighting, solar cells and optical displays because of their strong absorption in the near-ultraviolet (NUV) region and good intrinsic emissions originating from the electronic transitions of ${}^3\text{T}_J \rightarrow {}^1\text{A}_1$ ($J = 1, 2$) in the VO_4^{3-} group [17–20]. Besides, with the introduction of RE ions, the phonon-assisted energy transfer from the VO_4^{3-} group to RE ions can occur and the emissions arising from the VO_4^{3-} group and RE ions can be simultaneously observed in the RE ions doped vanadate material systems [21,22]. Hence, high-performance optical temperature sensors are expected to be realized in the RE ions doped vanadates. Unfortunately, to the best of our knowledge, the study on the optical thermometric behaviors of RE ions doped vanadates is still lacking. To figure out this shortage and extend the applications of vanadates, we chose the $\text{Ba}_3(\text{VO}_4)_2$ as the luminescent host material owing to its good photoluminescence (PL) properties and high stability [23]. Furthermore, considering the unique characteristic reddish-orange emissions of Sm^{3+} ions as well as the efficient energy transfer from VO_4^{3-} group to Sm^{3+} ions, it was selected as the dopant [24,25]. In this work, the Sm^{3+} -doped $\text{Ba}_3(\text{VO}_4)_2$ microparticles were constructed by a facile sol-gel technique and their phase structure, morphology and PL properties

were investigated. Ultimately, the temperature sensing behaviors of the resultant compounds were studied by analyzing the different temperature responses of VO_4^{3-} group and Sm^{3+} ions.

2. Experimental procedure

With the aid of the traditional citric acid-assisted sol-gel method, the $\text{Ba}_{3-3x}(\text{VO}_4)_2:3x\text{Sm}^{3+}$ ($\text{Ba}_3(\text{VO}_4)_2:3x\text{Sm}^{3+}$; $x = 0.00, 0.01, 0.04, 0.08, 0.13, 0.16$ and 0.20) microparticles were prepared. The starting materials including $\text{Ba}(\text{NO}_3)_2$ (99%), $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%), NH_4VO_3 (99.99%) and citric acid (99.5%) which were purchased from Sigma-Aldrich Co. were employed to synthesize the desired compounds. According to the designed chemical formula, $(3-3x)$ mmol $\text{Ba}(\text{NO}_3)_2$, $3x$ mmol $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 2 mmol NH_4VO_3 were weighted and dissolved in 200 ml of de-ionized water. Then, 10 mmol citric acid which acts as the chelating agent was added into the aforementioned solution. Subsequently, the beaker was sealed with a cover and kept at $80\text{ }^\circ\text{C}$ with strong mechanical stirring. When the solution color was changed from yellow to blue, the cover was removed and the mixture was continuously heated at $80\text{ }^\circ\text{C}$ to form a gray wet-gel. Afterwards, the wet-gel was moved to the oven and kept at $120\text{ }^\circ\text{C}$ for 12 h to create the gray xerogel. Finally, the xerogel was put in the alumina crucible and annealed at $1000\text{ }^\circ\text{C}$ for 6 h with an intermediate sintering at $650\text{ }^\circ\text{C}$ for 2 h . The final products were reground for further characterization.

The phase compositions of the studied compounds were identified by using a X-ray diffractometer (Bruker D8 Advance) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). The field-emission scanning electron microscope (FE-SEM) (LEO SUPRA 55, Carl Zeiss) equipped with an energy-dispersive X-ray (EDX) spectrum and transmission electron microscope (TEM; JEM-2100F) were employed to characterize the morphology behaviors of the synthesized products. The room-temperature luminescent spectra as well as the temperature-dependent PL emission spectra were recorded from a spectrofluorometer (Scinco FluoroMate FS-2). The temperature-controlled stage (NOVA ST540) was employed to adjust the temperature surrounding the resultant microparticles. The OriginPro 8.0 software was used to calculate the integrated PL emission intensity. The Fourier transform infrared (FT-IR) spectrum was detected by using a Thermo Nicolet-5700 FT-IR spectrophotometer.

3. Results and discussion

The X-ray diffraction (XRD) patterns of Sm^{3+} -doped $\text{Ba}_3(\text{VO}_4)_2$ microparticles at various dopant concentrations are shown in Fig. S1. It is evident that all the detected diffraction peaks were in agreement well with the standard Joint Committee on Powder Diffraction Standards (JCPDS) of card No. 29–0211 when $x \leq 0.08$, demonstrating that the studied samples exhibited pure rhombohedral phase. Nevertheless, with further introducing the Sm^{3+} ions into the host lattices, apart from the rhombohedral phase of $\text{Ba}_3(\text{VO}_4)_2$, some tiny peaks originating from the secondary phase of $\text{Ba}_2\text{SmV}_3\text{O}_{11}$ (JCPDS#45-0095) appeared (see Fig. S1), revealing that the Sm^{3+} ions had a solubility limitation in the $\text{Ba}_3(\text{VO}_4)_2$ host lattices. The FE-SEM and TEM were employed to characterize the morphology of the resultant samples. The FE-SEM and TEM images of typical $\text{Ba}_3(\text{VO}_4)_2:0.12\text{Sm}^{3+}$ microparticles, which are presented in Fig. 1(a) and (b), respectively, indicated that the Sm^{3+} -doped $\text{Ba}_3(\text{VO}_4)_2$ compounds consisted of aggregated and anomalous microparticles. This may be ascribed to the high synthetic temperature. Furthermore, it can be seen that the high resolution TEM (HR-TEM) image shown in Fig. 1(c) exhibited distinguishable lattice fringes and their average distance was estimated to be around 0.248 \AA which is assigned to the $(0\ 2\ 1)$ principal plane of $\text{Ba}_3(\text{VO}_4)_2$ (JCPDS#29-0211). As verified by the selective area electron diffraction (SAED) pattern (see Fig. 1(d)), clear dots were found in the particles, suggesting that the resultant samples were single crystalline in nature. Additionally, the elemental mapping results indicated that the elements presented in the $\text{Ba}_3(\text{VO}_4)_2:3x\text{Sm}^{3+}$ microparticles were homogeneously distributed, as

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