Journal of Solid State Chemistry 241 (2016) 99–104

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Ratiometric near infrared luminescent thermometer based on lanthanide metal-organic frameworks

Dan Yue, Jun Zhang, Dian Zhao, Xiusheng Lian, Yuanjing Cui *, Yu Yang, Guodong Qian *

State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 5 May 2016
Received in revised form
31 May 2016
Accepted 5 June 2016
Available online 7 June 2016

Keywords:
Near infrared luminescent
Lanthanide metal-organic frameworks
Physiological temperature sensing

ABSTRACT

A near infrared luminescent MOFs thermometer ($Nd_{0.676}Yb_{0.324}BTC$) was prepared via a simple solvothermal method using Ln^{3+} (Ln=Nd, Yb) ions and 1, 3, 5-benznenetricarboxylic acid (H_3BTC), and characterized by PXRD, TGA, ICP, and photoluminescence (PL) spectrum. These results indicate that the $Nd_{0.676}Yb_{0.324}BTC$ displays high relative sensitivity and excellent repeatability in the physiological temperature range (288–323 K), and the maximum relative sensitivity is determined to be 1.187% K^{-1} at 323 K. These NIR luminescent MOFs may have potential applications in physiological temperature sensing.

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1. Introduction

Metal–organic frameworks (MOFs) have high surface area, large pore volume and widely tunable composition, which make them useful for startling performances in gas storage and separation, catalysis, nonlinear optics, and biomedicine [1–16]. Recently, through the great variety of structural design, pore size control and post-synthetic modification, numerous MOFs with abundant and tunable luminescent properties have been prepared [17–22]. Among them, Lanthanide metal–organic frameworks (Ln-MOFs), with fast response and high sensitivity, have been explored and realized for functionalities and applications in display, sensing, and luminescent thermometers [23–27]. For example, the first ratiometric luminescent MOF thermometer, $Eu_{0.0069}Tb_{0.9931}$-DMBDC (DMBDC=2, 5-dimethoxy-1, 4-benzendicarboxylate) was synthesized. As a result of the strong sensitizing ability of the ligand and the energy transfer from Tb^{3+} to Eu^{3+}, this mixed MOF thermometer exhibits an excellent linear correlation between temperature and luminescence intensity ratio from 50 to 200 K [28]. Building upon this work, nanorods of $Tb_{0.99}Eu_{0.01}(BDC)_{1.5}(H_2O)_2$ (BDC=1-4-benzendicarboxylate) have been prepared. These nanoMOFs display an outstanding performance as ratiometric luminescent thermometers in the physiological temperature range (300–320 K) [29].

As expected, utilizing Ln-MOFs to explore temperature sensing has aroused great interest. Particularly, the near infrared luminescent MOFs have several emissive properties that are highly desirable for biomedical analysis due to their ability of converting NIR light to visible light. NIR MOFs have unique advantages for living cells for NIR imaging and barcoded luminescent materials. They exhibit sharp, nonoverlapping, and easily identifiable emission bands [30–32]. In contrast to other Ln-MOFs, NIR luminescent MOFs have several outstanding features. Compared with UV excitation source, the NIR excitation source offers a substantially higher tissue penetration depth and causes less damage to biological samples, and improves the signal-to-noise ratio and sensitivity in biological detection [33–35]. Thus it is highly desirable but challenging to develop a facile strategy for controllable synthesis of NIR luminescent MOFs. We have demonstrated the first near infrared luminescent MOF thermometer, $Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$, and it displays near infrared fluorescence and excellent sensitivity in the physiological temperature range (293–313 K) [36]. In order to further improve the sensitivity of NIR luminescent MOFs thermometer, we synthesized another NIR luminescent MOFs with the utilizing of the H_3BTC. As a simple ligand, H_3BTC has been investigated for the construction of functional MOFs. Because H_3BTC has three carboxyl groups which exhibit versatile coordination and may be deprotonated to compensate for the charge [37]. Therefore, the rigid triangle backbone and versatile coordination modes of H_3BTC could benefit the assembly of NIR luminescent MOFs.

In this work, we synthesized three NIR luminescent MOFs: $[Nd(BTC)(H_2O)]\cdot 5H_2O$ (NdBTC), $[Yb(BTC)(H_2O)]\cdot 5H_2O$ (YbBTC), and $[Nd_{0.676}Yb_{0.324}BTC)(H_2O)]\cdot 5H_2O$ ($Nd_{0.676}Yb_{0.324}BTC$) based on H_3BTC. Study attention is paid to the investigation of their NIR luminescence properties, and luminescent analysis indicates that $Nd_{0.676}Yb_{0.324}BTC$ displays high relative sensitivity in the

* Corresponding authors.
E-mail addresses: cuiyj@zju.edu.cn (Y. Cui), gdqian@zju.edu.cn (G. Qian).

http://dx.doi.org/10.1016/j.jssc.2016.06.005
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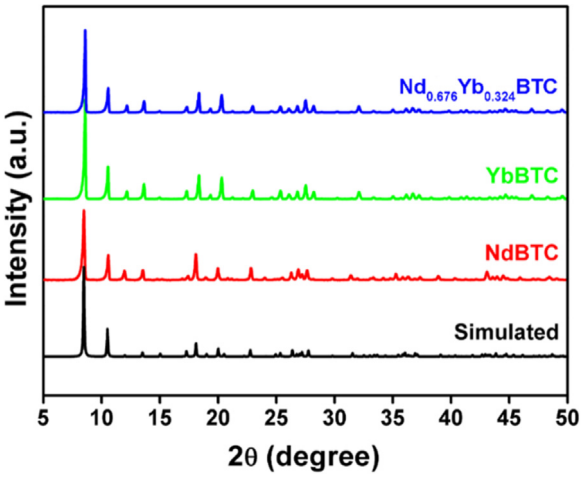

Fig. 1. PXRD patterns of NdBTC, YdBTC, and $Nd_{0.676}Yb_{0.324}BTC$.

physiological temperature range (288–323 K).

2. Experimental section

2.1. Materials and measurements

All chemicals were used directly without further purification. 1, 3, 5-benznenetricarboxylic acid (H_3BTC) was purchased from J&K Chemicals (Shanghai, China). $Nd(NO_3)_3 \cdot 6H_2O$ and $Yb(NO_3)_3 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The synthesis of NdBTC is thus presented here in detail as a representative: A mixture of $Nd(NO_3)_3 \cdot 6H_2O$ (0.657 g, 1.5 mmol), H_3BTC (0.350 g, 1.67 mmol), DMF (60 mL), H_2O (20 mL), and 12 mol L^{-1} HCl (2 mL) was added to a 100 mL glass vial. The mixture solution was stirred for 2 h, and the resulting solution was kept at 85 °C for 24 h. After the vial was cooled to room temperature naturally, purple needle-like crystals were grown and can be collected by filtration and washed with DMF. Additionally, YbBTC and $Nd_{0.676}Yb_{0.324}BTC$ were synthesized similarly to NdBTC except for using a mixture containing the desired lanthanide nitrate.

2.2. Characterization

Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 5–50°$ range on an X'Pert PRO diffractometer with Cu Kα ($\lambda = 1.542$ Å) radiation at room temperature. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 heated from room temperature to 800 °C under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Inductively coupled plasma spectroscopy (ICP) was performed on a Thermo IRIS Intrepid II XSP spectrometer. The emission spectra for the samples were recorded by a Edinburgh Instrument F920 fluorescence spectrometer using 808 nm laser as the light source. The temperature-dependent emission spectra were recorded by a Edinburgh Instrument F920

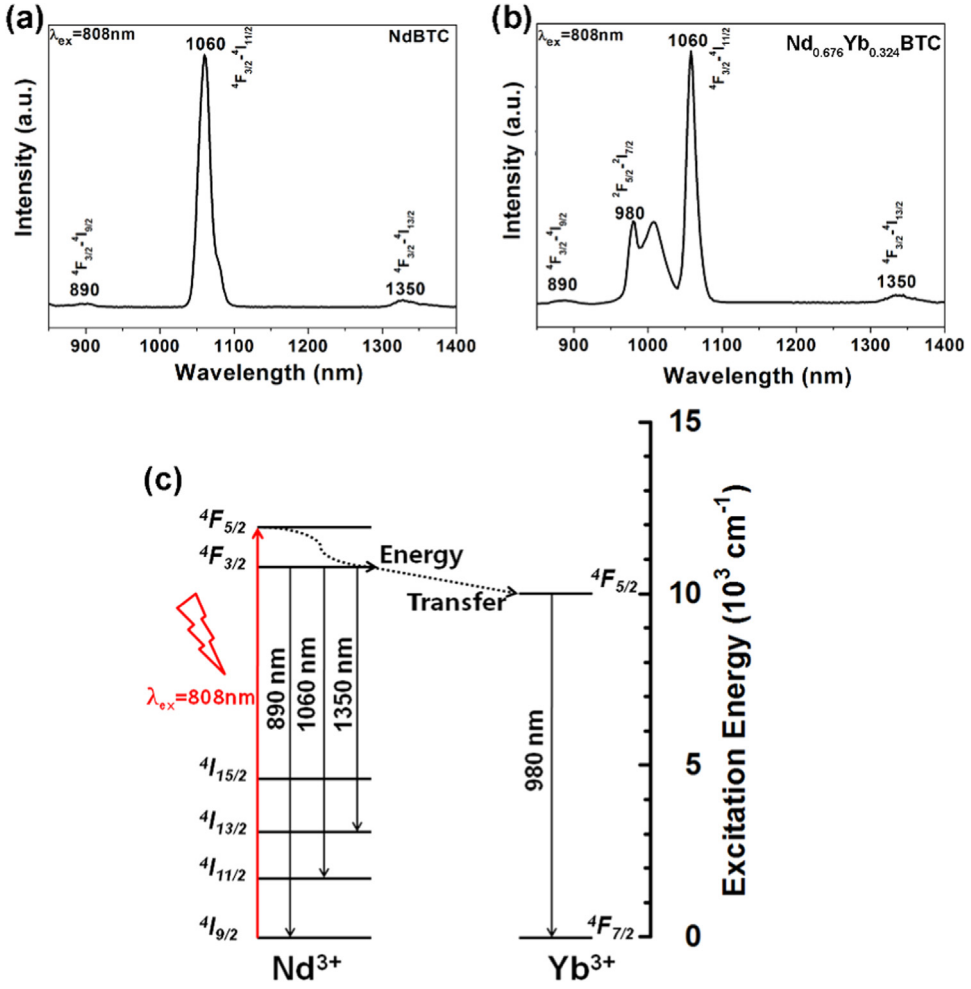

Fig. 2. Emission spectra of (a) NdBTC; (b) $Nd_{0.676}Yb_{0.324}BTC$ excited at 808 nm, (c) Energy level scheme and the energy transfer process from Nd^{3+} to Yb^{3+}.

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