Unraveling the Electronic Structures of Neodymium in LiLuF₄ Nanocrystals for Ratiometric Temperature Sensing

Ping Huang, Wei Zheng,* Datao Tu, Xiaoying Shang, Meiran Zhang, Renfu Li, Jin Xu, Yan Liu, and Xueyuan Chen*

Nd³⁺-doped near-infrared (NIR) luminescent nanocrystals (NCs) have shown great promise in various bioapplications. A fundamental understanding of the electronic structures of Nd³⁺ in NCs is of vital importance for discovering novel Nd³⁺-activated luminescent nanoprobes and exploring their new applications. Herein, the electronic structures of Nd³⁺ in LiLuF₄ NCs are unraveled by means of low-temperature and high-resolution optical spectroscopy. The photoactive site symmetry of Nd³⁺ in LiLuF₄ NCs and its crystal-field (CF) transition lines in the NIR region of interest are identified. By taking advantage of the well-resolved and sharp CF transition lines of Nd³⁺, the application of LiLuF₄:Nd³⁺ NCs as sensitive NIR-to-NIR luminescent nanoprobes for ratiometric detection of cryogenic temperature with a linear range of 77–275 K is demonstrated. These findings reveal the great potential of LiLuF₄:Nd³⁺ NCs in temperature sensing and also lay a foundation for future design of efficient Nd³⁺-based luminescent nanoprobes.

1. Introduction

Trivalent neodymium (Nd³⁺) ion doped luminescent nanocrystals (NCs) have recently attracted considerable attention owing to their superior optical properties in the near-infrared (NIR) spectral region.¹ These Nd³⁺-doped NCs are able to emit NIR light under excitation with a low-cost 808 nm diode laser, which feature a series of advantages such as large penetration depth, minimal background interference, and little damage to the targeted samples, and thus are regarded as excellent NIR-to-NIR luminescent nanoprobes for various bioapplications.² Specifically, Nd³⁺-doped NCs have been frequently used as sensitive nanothermometers for physiological temperature sensing in tissues based on the temperature-dependent energy transfer with other lanthanide (Ln³⁺) activators or the electronic transitions from the thermally coupled crystal-field (CF) energy levels of Nd³⁺.[³] Nonetheless, the CF transition lines of Nd³⁺-doped NCs are usually elusive and undistinguishable at physiological temperatures because of the line broadening and multiple sites of Nd³⁺ in NCs.⁴ As a result, the assignment of CF transition lines in previously reported Nd³⁺-based nanothermometer had to rely on the reference of CF levels of bulk analogs, which could be unreliable and lead to an artificial detection result. Therefore, it is urgent to unravel the electronic structures of Nd³⁺ in NCs and assign its CF transition lines in the NIR of interest, which is of fundamental significance for designing novel Nd³⁺-activated luminescent nanoprobes and exploring their new applications.

Lithium lutetium tetrafluoride (LiLuF₄), owing to its low phonon energy and high chemical stability, is an excellent host material for Nd³⁺ doping to produce efficient upconverting and downshifting luminescence.[⁶] Nd³⁺-activated LiLuF₄ bulk crystals have been documented as efficient solid-state laser crystals,[⁷] and their nanoscale counterparts have been reported as sensitive NIR-to-NIR luminescent nanoprobes for subsurface bioimaging.[⁶] Moreover, the luminescence of Nd³⁺ in LiLuF₄ lattice is characterized by sharp emission peaks even at room temperature due to the strong CF level splitting,⁶ which facilitates the discrimination of the CF transition lines of Nd³⁺ in NIR and thereby enables the assignment of CF energy levels of Nd³⁺ in nanoscale LiLuF₄.

Herein, we report for the first time the electronic structures of Nd³⁺ in LiLuF₄ NCs. We first use Eu³⁺ ion as the structural probe to unveil the local site symmetry of Ln³⁺ dopants in LiLuF₄ NCs by means of high-resolution photoluminescence (PL) spectroscopy, time-resolved PL (TRPL) spectroscopy, and site-selective PL spectroscopy at 10 K. With definite local site symmetry, we then assign the CF transition lines of Nd³⁺ in the NIR region and the corresponding CF levels through temperature-dependent PL spectroscopy. Furthermore, by taking advantage of the well-resolved CF transition lines from the thermally coupled Stark sublevels of ⁴F₃/₂ of Nd³⁺, we show the application of LiLuF₄:Nd³⁺ NCs as NIR-to-NIR luminescent nanoprobes.

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Herein, we report for the first time the electronic structures of Nd³⁺ in LiLuF₄ NCs. We first use Eu³⁺ ion as the structural probe to unveil the local site symmetry of Ln³⁺ dopants in LiLuF₄ NCs by means of high-resolution photoluminescence (PL) spectroscopy, time-resolved PL (TRPL) spectroscopy, and site-selective PL spectroscopy at 10 K. With definite local site symmetry, we then assign the CF transition lines of Nd³⁺ in the NIR region and the corresponding CF levels through temperature-dependent PL spectroscopy. Furthermore, by taking advantage of the well-resolved CF transition lines from the thermally coupled Stark sublevels of ⁴F₃/₂ of Nd³⁺, we show the application of LiLuF₄:Nd³⁺ NCs as NIR-to-NIR luminescent nanoprobes.
nanoprobes for ratiometric detection of cryogenic temperature with high reliability and sensitivity, thereby revealing the great potential of LiLuF₄:Nd³⁺ NCs for temperature sensing.

2. Results and Discussion

The LiLuF₄ crystal has a scheelite structure (space group I₄₁/a) with Lu⁺⁺ ions surrounded by eight F⁻ ions that form the edges of a slightly distorted dodecahedron. All Lu⁺⁺ ions occupy a single crystallographic site of S₄ symmetry (Figure 1a). High-quality LiLuF₄:Ln³⁺ (Ln = Eu and Nd) NCs were synthesized through a thermal decomposition method as we previously reported.[6b] The as-synthesized NCs are hydrophobic and can be readily dispersed in a variety of nonpolar organic solvents such as cyclohexane. X-ray diffraction (XRD) patterns (Figure 1b) show that all diffraction peaks of the NCs can be well indexed into tetragonal LiLuF₄ (JCPDS No. 027-1251) without any additional impurities. Transmission electron microscopy (TEM) images show that both LiLuF₄:2%Nd³⁺ and LiLuF₄:5%Eu³⁺ NCs are rhomboid with mean sizes of (28.4 ± 1.2) × (33.1 ± 1.5) and (28.0 ± 0.9) × (34.2 ± 1.0) nm, respectively (Figure 1c–e). High-resolution TEM images (insets of Figure 1c,d) exhibit clear lattice fringes with an observed d spacing of 0.46 nm for the (101) plane of tetragonal LiLuF₄, confirming pure phase and high crystallinity of the resulting NCs. Compositional analyses through energy-dispersive X-ray spectrum and inductively coupled plasma-atomic emission spectroscopy reveal 1.8 mol% of Nd³⁺ and 4.6 mol% of Eu³⁺ in LiLuF₄ matrix (Figure S1, Supporting Information), which are generally consistent with their nominal dopant concentrations (2 mol% of Nd³⁺ and 5 mol% of Eu³⁺).

Eu³⁺ ion is a sensitive spectroscopic probe, which can provide site symmetry information because of its nondegenerate emissive state of 5D₀ and the ground state of 7F₀.[8] To probe the practical local site symmetry of Ln³⁺ dopants in LiLuF₄ NCs, we measured the high-resolution PL spectra of Eu³⁺ in LiLuF₄ NCs. Emission and excitation spectra and PL decays were recorded at 10 K to avoid thermal broadening of spectral lines at room temperature (Figure S2, Supporting Information).[9] Figure 2 shows the high-resolution PL spectra of LiLuF₄:5%Eu³⁺ NCs at 10 K, which enables a detailed assignment of the CF transition lines of Eu³⁺. By monitoring the Eu³⁺ emission at 613.8 nm, a series of CF transition lines of Eu³⁺ from the 7F₀ ground state to the excited multiplets (5D₁, 5L₁, 5G₁, 5H₁, and 5F₁) were observed (Figure 2a).[10] Upon excitation to 5Lᵃ of Eu³⁺ at 393.0 nm, the CF emission peaks from 5D₀ and 5D₁ to 7Fᵃ (J = 0, 1, 2, 3, and 4) with full-width at half-maximum (FWHM) smaller than 0.5 nm were detected (Figure 2b). PL decay measurements show that both 5D₀ and 5D₁ display a single exponential decay with PL lifetimes of 11.3 and 2.7 ms, respectively (Figure 2c), suggesting a homogeneous CF environment around Ln³⁺ dopants in LiLuF₄ lattice.[11] The distinct PL lifetimes of 5D₀ and 5D₁ allow us to distinguish the emission peaks of 5D₀ from those of 5D₁ by means of TRPL spectroscopy. Figure 2d shows the TRPL spectra of LiLuF₄:5%Eu³⁺ NCs at 10 K with different...
delay times. It was observed that the emission peaks from the short-lived $^5D_1$ level declined gradually with increasing the delay time and totally vanished when the delay time was longer than 6 ms, while the emission peaks from the long-lived $^5D_0$ level remained explicitly observed in the TRPL spectra even at a delay time of 10 ms. As a result, total numbers of 0, 2, 3, 4, and 4 CF transition lines of Eu$^{3+}$ from $^5D_0 \rightarrow ^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$ can be discerned in LiLuF$_4$ NCs. To check whether all these transition lines arise from the same site, site-selective excitation spectra were measured by monitoring the three peaks of $^5D_0 \rightarrow ^7F_2$ at 610.4, 613.8, and 620.8 nm. The obtained excitation spectra were coincident (Figure S3, Supporting Information), indicating that the PL originated from Eu$^{3+}$ ions occupying a single spectroscopic site, as also evidenced by the essentially identical site-selective emission spectra upon excitation to $^5L_6$ at 393.0, 395.8, 399.4, and 400.6 nm (Figure 2e and Figure S4, Supporting Information). According to the branching rules and the transition selection rules of the 32 point groups (Table S1, Supporting Information),[8b,c] the spectroscopic site symmetry of Eu$^{3+}$ in LiLuF$_4$ NCs was determined to be $S_4$, which agrees well with the crystallographic site symmetry of Lu$^{3+}$ in LiLuF$_4$. These results suggest that Ln$^{3+}$ ions are prone to occupy a single spectroscopic site of $S_4$ symmetry in LiLuF$_4$ NCs at low doping levels (<5 mol%) due to the close ionic radii and chemical properties of Ln$^{3+}$ ions.

With definite local site symmetry of Ln$^{3+}$ dopants, we are able to assign the CF transition lines of Nd$^{3+}$ in LiLuF$_4$ NCs by means of high-resolution PL spectroscopy. Figure 3a shows the PL excitation spectrum of Nd$^{3+}$ in LiLuF$_4$ NCs at 10 K by monitoring the Nd$^{3+}$ emission at 1053.2 nm, from which a series of CF transition lines of Nd$^{3+}$ from the $^4I_{9/2}$ ground state to the excited multiplets ($^4F_J$, $^4H_J$, $^4S_J$, $^2G_J$, $^2G_J$, $^2D_J$, and $^2D_J$) were identified.[12] Specifically, two excitation peaks at 861.4 and 865.9 nm were clearly observed (inset of Figure 3a), ascribing to the CF transitions of Nd$^{3+}$ from the $^4I_{9/2}$ ground state to the upper ($R_2$) and lower ($R_1$) Stark sublevels of $^4F_{3/2}$, respectively. This implies that the CF levels of Nd$^{3+}$ are doubly degenerate in LiLuF$_4$ NCs, as expected for a Kramers ion.[13] 10 K PL emission spectrum (Figure 3b) shows that the NCs exhibit a set of characteristic and sharp emission peaks (FWHM < 0.9 nm) from the two Stark sublevels of $^4F_{3/2}$ ($R_1$ and $R_2$) Stark sublevels of $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ of Nd$^{3+}$ under xenon lamp excitation at 791.3 nm. To confirm that all these transition lines arise from a single site, we recorded PL emission spectrum of the NCs by exciting them with an 808 nm diode laser, whereby all possible spectroscopic sites of Nd$^{3+}$ could be excited in view of the high power density (50 W cm$^{-2}$) and relatively wide FWHM (3.2 nm) of the laser source (Figure S5, Supporting Information). It turned out that the emission pattern of the NCs under 808 nm diode laser excitation was exactly identical to that under xenon lamp excitation at 791.3 nm (Figure S6, Supporting Information), inferring that the PL originates from Nd$^{3+}$ ions occupying a single spectroscopic site. From the emission spectrum, total numbers of 10, 12, and 14 CF transition lines of Nd$^{3+}$ from $^4F_{3/2}$ to $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ were discerned, which agree well...
with the theoretically predicted numbers for Nd$^{3+}$ in LiLuF$_4$ with doubly degenerate CF levels.$^{[13]}$ These results demonstrate unambiguously that Nd$^{3+}$ ions occupy a single spectroscopic site of $S_4$ symmetry in LiLuF$_4$ NCs, as revealed by using Eu$^{3+}$ as the structural probe.

Because the energy difference between the R$_1$ and R$_2$ Stark sublevels of $^4F_{3/2}$ is only 58 cm$^{-1}$, the higher Stark sublevel (R$_2$) is easily thermally populated from the lower one (R$_1$). As a result, PL intensity ratio between the emissions from R$_2$ and R$_1$ would increase with the temperature rise, enabling discrimination of the CF transition lines of R$_2$ from those of R$_1$ through the temperature-dependent PL emission spectra (Figure 3c). It was observed that the intensities of the CF emission peaks at 861.9, 872.2, 875.7, 882.3, and 904.9 nm increased significantly with the temperature rise, corresponding to the transitions from the R$_2$ sublevel of $^4F_{3/2}$ to the five CF levels (Z$_1$, Z$_2$, Z$_3$, Z$_4$, and Z$_5$) of $^4I_{9/2}$ (Figure 3d). By contrast, the intensities of the CF emission peaks at 866.2, 876.9, 880.4, 886.4, and 909.8 nm showed only a slight increase with the temperature rise, corresponding to the transitions from the R$_1$ sublevel of $^4F_{3/2}$. The slight increase in R$_1$ lines is caused by the spectral overlap with R$_2$ lines. Based on the defined

Figure 3. a) 10 K PL excitation spectrum of LiLuF$_4$:2%Nd$^{3+}$ NCs by monitoring the Nd$^{3+}$ emission at 1053.2 nm and b) their emission spectrum upon excitation at 791.3 nm. The inset in (a) shows two CF transition lines from the $^4I_{9/2}$ ground state to the upper and lower Stark sublevels of $^4F_{3/2}$. c) Temperature-dependent PL emission spectra (10–300 K) for the $^4F_{3/2}$→$^4I_{J}$ ($J = 9/2, 11/2,$ and $13/2$) CF transitions of Nd$^{3+}$ in LiLuF$_4$ NCs upon 808 nm diode laser excitation at a power density of 1 W cm$^{-2}$. The spectra were normalized at the maximum intensities around 880.4, 1053.1, and 1325.1 nm for the emissions from $^4F_{3/2}$ to $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$, respectively. The dashed lines denote the CF transitions from the R$_1$ (black) and R$_2$ (red) Stark sublevels of $^4F_{3/2}$ to those of $^4I_{J}$. d) CF energy levels of the $^4F_{3/2}$ and $^4I_{J}$ multiplets of Nd$^{3+}$ in LiLuF$_4$ NCs, showing all CF transitions observed in (c).
CF transition lines, the CF levels of $^4I_{9/2}$ can be unequivocally identified, as listed in Table 1. Similarly, CF transition lines from the $R_1$ and $R_2$ sublevels of $^4F_{3/2}$ to those of $^4I_{11/2}$ and $^4I_{13/2}$ can be specified by virtue of the temperature-dependent PL emission spectra, from which the CF levels of $^4I_{11/2}$ and $^4I_{13/2}$ were experimentally assigned (Table 1). Besides, we also found a redshift in CF transition lines of Nd$^{3+}$ with the temperature rise, especially for the transitions from $R_2$ of $^4F_{3/2}$ to $Z_1$ and $Z_2$ of $^4I_{11/2}$ (Figure 3c), as a result of enhanced electron-phonon coupling at higher temperatures. Importantly, we found that the CF transition lines from the thermally coupled $R_1$ and $R_2$ Stark sublevels of $^4F_{3/2}$ to $Z_1$ of $^4I_{9/2}$ at 862 nm ($R_2\rightarrow Z_1$) and 866 nm ($R_1\rightarrow Z_1$) are well resolved with little interference from other Stark components at temperatures below 300 K. This feature makes LiLuF$_4$:Nd$^{3+}$ NCs an ideal nanoprobe candidate for ratiometric luminescent detection of temperature below 300 K by using the temperature-dependent PL intensity ratio between the $R_2\rightarrow Z_1$ and $R_1\rightarrow Z_1$ transitions at 862 and 866 nm ($I_{862}/I_{866}$), respectively. To validate the applicability of LiLuF$_4$:Nd$^{3+}$ NCs for temperature sensing, we deconvoluted the $^4F_{3/2}\rightarrow^4I_{9/2}$ emission spectra of Nd$^{3+}$ into ten Gaussian components according to the CF transitions between their Stark sublevels (Figure 4a), from which the PL intensity ratio between $R_2\rightarrow Z_1$ and $R_1\rightarrow Z_1$ ($I_{862}/I_{866}$) was derived. Further temperature-correlated PL emission spectra showed that the PL intensity ratio $I_{862}/I_{866}$ increased gradually with increasing the temperature from 77 to 575 K (Figure S7, Supporting Information), as a result of enhanced thermal population of the $R_2$ sublevel from the $R_1$ sublevel of $^4F_{3/2}$ at higher temperatures. Specifically, the ratio of $I_{862}/I_{866}$ displayed a linear dependence on temperature in the range of 77–275 K, with its value increased from 1.46 at 77 K to 3.23 at 275 K (Figure 4b). Moreover, such temperature evolution of $I_{862}/I_{866}$ was found to be reversible during the heating and cooling cycle between 77 and 275 K. The ratios of $I_{862}/I_{866}$ recorded at 77, 175, and 275 K were nearly unchanged with deviations smaller than 0.5% over a span of 20 cycles of heating and cooling processes.

Table 1. Experimental energy levels for the $^4I$ and $^4F_{3/2}$ multiplets of Nd$^{3+}$ in LiLuF$_4$ NCs.

| Multiplet | Energy [cm$^{-1}$] | Multiplet | Energy [cm$^{-1}$] | Multiplet | Energy [cm$^{-1}$] | Multiplet | Energy [cm$^{-1}$] |
|-----------|-----------------|-----------|-----------------|-----------|-----------------|-----------|-----------------|
| $^4I_{9/2}$ | 0               | $^4I_{11/2}$ | 2003            | $^4I_{13/2}$ | 3948            | $^4F_{3/2}$ | 11 544          |
| 138       | 2041            | 3978      | 11 602          |
| 183       | 2047            | 3996      |                 |
| 255       | 2086            | 4027      |                 |
| 549       | 2241            | 4222      |                 |
| 2283      |                 | 4254      |                 |
|           |                 | 4266      |                 |

Figure 4. a) PL emission spectrum for the $^4F_{3/2}\rightarrow^4I_{9/2}$ transitions of Nd$^{3+}$ in LiLuF$_4$ NCs at 275 K and its Gaussian fit according to the CF transitions. b) PL intensity ratio between the $R_2\rightarrow Z_1$ and $R_1\rightarrow Z_1$ CF transitions at 862 and 866 nm ($I_{862}/I_{866}$) as a function of temperature during a heating and cooling cycle between 77 and 275 K. Each data point represents the mean ($\pm$standard deviation) of three independent measurements. c) Variation of the intensity ratio $I_{862}/I_{866}$ recorded at 77, 175, and 275 K measured over a span of 20 cycles of heating and cooling processes. d) The relative temperature sensitivity ($S_r$) of LiLuF$_4$:2%Nd$^{3+}$ nanoprobes as a function of temperature. The error bars result from error propagation in the determination of $S_r$. 

Adv. Sci. 2019, 6, 1802282 © 2019 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
The unambiguous revelation of photoactive site symmetry and detection of temperature with a wide linear range of 77–275 K. as sensitive NIR-to-NIR luminescent nanoprobes for ratiometric lines, and high photostability of LiLuF$_4$:Nd$^{3+}$ single photoactive site symmetry, well-resolved CF transition probes. In this regard, the superior features combined with the 4 symmetry for Ln$^{3+}$ dopants was identified in LiLuF$_4$ NCs, which is consistent with the crystallographic site symmetry of Lu$^{3+}$ in LiLuF$_4$ lattice. By means of temperature-dependent PL spectroscopy, a total number of 36 CF transition lines of Nd$^{3+}$ in LiLuF$_4$ NCs in the NIR region were unequivocally assigned. Furthermore, by employing the sharp and well-resolved CF transitions from the thermally coupled Stark sublevels of $^4$I$_{13/2}$ of Nd$^{3+}$, we have demonstrated the application of LiLuF$_4$:Nd$^{3+}$ NCs as sensitive NIR-to-NIR luminescent nanoprobes for ratiometric detection of temperature with a wide linear range of 77–275 K. The unambiguous revelation of photoactive site symmetry and electronic structures of Nd$^{3+}$ in inorganic NCs is of vital importance for future design and development of Nd$^{3+}$-based NIR luminescent nanoprobes toward versatile applications such as cryogenic temperature sensing for space and energy exploration.

4. Experimental Section

**Chemicals and Materials:** Lu$_2$O$_3$ (99.99%), Eu$_2$O$_3$ (99.99%), Nd$_2$O$_3$ (99.99%), oleic acid (OA, 90%), oleylamine (OAm, 90%), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich (Shanghai, China). CF$_3$COOLi·H$_2$O (99.99%), trifluoroacetic acid (≥99.0%), ethanol (≥99.5%), acetone (≥99.5%), and cyclohexane (≥99.5%) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Lu(CF$_3$COO)$_3$, Eu(CF$_3$COO)$_3$, and Nd(CF$_3$COO)$_3$ were prepared by dissolving Lu$_2$O$_3$, Eu$_2$O$_3$, and Nd$_2$O$_3$, respectively, in trifluoroacetic acid at 90 °C. All the chemical reagents were used as received without further purification.

**Synthesis of LiLuF$_4$:Ln$^{3+}$ NCs:** Monodisperse LiLuF$_4$:Ln$^{3+}$ NCs (Ln = Eu or Nd) were synthesized through a thermal decomposition method. In a typical synthesis of LiLuF$_4$:2%Nd$^{3+}$ NCs, 1 mmol of CF$_3$COOLi·H$_2$O, 0.98 mmol of Lu(CF$_3$COO)$_3$, and 0.02 mmol of Nd(CF$_3$COO)$_3$ were mixed with 6 mL of OA, 2 mL of OAm, and 2 mL of ODE in a 100 mL three-neck round-bottom flask. The resulting mixture was heated to 120 °C under N$_2$ flow with constant stirring for 30 min to form a clear yellowish solution. Thereafter, the resulting solution was heated to 320 °C under N$_2$ flow with vigorous stirring for 40 min and then cooled down to room temperature. The obtained NCs were precipitated by addition of 20 mL of acetone, collected by centrifugation, washed with ethanol several times, and finally dried in vacuum at 60 °C for 24 h.

**Structural and Optical Characterization:** Powder XRD patterns of the samples were collected with an X-ray diffractometer (MiniFlex2, Rigaku) using Cu Kα1 radiation (λ = 0.154187 nm). Both the low- and high-resolution TEM measurements were performed using a Tecnai G2 F20 TEM equipped with an energy-dispersive X-ray spectrometer. Inductively coupled plasma (ICP) analysis was conducted by using Inductively Coupled Plasma AES spectrometer (Ultima2, Jobin Yvon). PL excitation and emission spectra and PL decays were recorded on an Edinburgh Instruments FLS920 spectrometer equipped with both continuous (450 W) and pulsed xenon lamp at room temperature. For low temperature measurement, samples were mounted on a closed cycle cryostat (10–350 K, DE202, Advanced Research Systems). The emission or excitation monochromator’s slits were set as small as possible to maximize the instrumental resolution, and the highest wavelength resolution is 0.05 nm. The line intensities and positions of the measured spectra were calibrated according to the correction curve of the instrument and standard mercury lamp.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the Strategic Priority Research Program of the CAS (KDB200000000), the NSFC (Nos. U1805252, 217171185, 21501180, 21875250, and 11774345), the CAS/SSAFEA International Partnership Program for Creative Research Teams, the Youth Innovation Promotion Association (No. 2016277), the Chunniao Project of Haixi Institutes of the CAS (No. CMZX-2016-002), and Natural Science Foundation of Fujian Province (Nos. 2017J05095, 2017J0018, and 2018J01089).

Conflict of Interest

The authors declare no conflict of interest.
Keywords
energy level, LiLuF₄ nanocrystals, neodymium, site symmetry, temperature sensing

Received: December 17, 2018
Revised: February 18, 2019
Published online: March 14, 2019

[1] a) Y.-F. Wang, G.-Y. Liu, L.-D. Sun, J.-W. Xiao, J.-C. Zhou, C.-H. Yan, ACS Nano 2013, 7, 7200; b) X. Xie, N. Gao, R. Deng, Q. Sun, Q.-H. Xu, X. Liu, J. Am. Chem. Soc. 2013, 135, 12608; c) Y. Zhong, G. Tian, Z. Gu, Y. Yang, L. Gu, Y. Zhao, Y. Ma, J. Yoo, Adv. Mater. 2014, 26, 2831; d) F. Lu, L. Yang, Y. Ding, J.-J. Zhu, Adv. Funct. Mater. 2016, 26, 4778; e) J. T. Xu, P. P. Yang, M. D. Sun, H. T. Bi, B. Liu, D. Yang, S. L. Gai, F. He, J. Lin, ACS Nano 2017, 11, 4133; f) B. del Rosal, U. Rocha, E. C. Ximendes, E. M. Rodriguez, D. Jaque, J. G. Sole, Opt. Mater. 2017, 63, 185; g) D. Hreniak, W. Strek, Adv. Funct. Mater. 2018, 28, 10; h) Z. S. Yu, Y. Z. Xia, J. Xing, Z. H. Li, J. J. Zhen, Y. H. Jin, Y. C. Tian, C. Liu, Z. Q. Jiang, L. A. G. Wu, Nanoscale 2017, 9, 101703.

[2] a) G. Chen, T. Y. Ohulchanskyi, S. Liu, W.-C. Law, F. Wu, Adv. Funct. Mater. 2014, 5, a) D. Wawrzynczyk, A. Bednarkiewicz, M. Nyk, W. Strek, M. Samoc, Nanoscale 2013, 4, 6959; b) L. Marciniak, A. Bednarkiewicz, D. Hreniak, W. Strek, J. Mater. Chem. C 2016, 4, 11284; c) A. Benayas, B. del Rosal, A. Perez-Delgado, K. Santacruz-Gomez, D. Jaque, G. A. Hirta, F. Vetrone, Adv. Opt. Mater. 2015, 3, 687.

[3] a) I. R. Martin, Y. Goyot, M. F. Joubert, R. Y. Abdulsabirov, S. L. Korableva, V. V. Semashko, J. Alloys Compd. 2001, 323, 763; b) P. Huang, W. Zheng, S. Y. Zhou, D. T. Zu, Z. Chen, H. M. Zhu, R. F. Li, E. Ma, M. D. Huang, X. Y. Chen, Angew. Chem., Int. Ed. 2014, 53, 1252; c) X. S. Zhai, P. P. Li, P. Zhang, Z. Wang, S. Y. Song, X. Xu, X. L. Liu, J. Feng, H. J. Zhang, Biomaterials 2015, 65, 115; d) Q. S. Qin, P. Z. Zhang, L. D. Sun, S. Shi, N. X. Chen, H. Dong, X. Y. Zheng, L. M. Li, C. H. Yan, Nanoscale 2017, 9, 4660; e) J. Liu, H. Rijckaert, M. Zeng, K. Haustreuer, B. Lafort, L. Vincze, I. Van Driessche, A. M. Kaczmarek, R. Van Deun, Adv. Funct. Mater. 2018, 28, 10; f) Z. S. Yu, Y. Z. Xia, J. Xing, Z. H. Li, J. J. Zhen, Y. H. Jin, Y. C. Tian, C. Liu, Z. Q. Jiang, L. A. G. Wu, Nanoscale 2017, 9, 101703.

[4] a) C. C. Zhao, Y. Hang, L. H. Zhang, X. M. He, J. G. Yin, R. Li, T. Yu, W. B. Chen, Laser Phys. Lett. 2011, 8, 263; b) P. Peixiong, W. Youbao, Y. Jigang, Z. Lianhan, Z. Chengchun, L. Hongqiang, Z. Rui, X. Jianqiu, L. Youchen, H. Yin, Laser Phys. Lett. 2014, 11, 115803.

[5] a) H.-I. Wen, G. H. jia, C. K. Duan, P. A. Tanner, Phys. Chem. Chem. Phys. 2010, 12, 9933; b) G. H. jia, P. A. Tanner, C. K. Duan, J. Despert-Chys, J. Phys. Chem. C 2010, 114, 2769; c) P. A. Tanner, Chem. Soc. Rev. 2013, 42, 5090; d) D. Tu, W. Zheng, P. Huang, X. Chen, Coord. Chem. Rev. 2019, 378, 104.

[6] a) A. Ellens, H. Andres, A. Meijerink, G. Blassie, Phys. Rev. B 1997, 55, 173; b) A. Ellens, H. Andres, M. L. H. terHeerdt, R. T. Wegh, A. Meijerink, G. Blassie, Phys. Rev. B 1997, 55, 180.

[7] a) C. Gorrilerwalrand, K. Binnemans, L. Fluyt, J. Phys.: Condens. Matter 1993, 5, 8359; b) D. Jaque, J. G. Sole, D. Jaque, Nano Res. 2014, 10, 1141; c) R. Wang, X. Li, L. Zhou, F. Zhang, Angew. Chem., Int. Ed. 2014, 53, 12086; d) I. Villa, A. Vedda, M. Pedroni, F. Vetrone, D. Ma, F. Sanz-Rodriguez, Adv. Mater. 2018, 30, 126674; e) Z. L. Xue, S. J. Zeng, J. H. Hao, Biomaterials 2018, 171, 153; f) Y. Fan, P. Yang, W. Q. Sun, L. Zhang, L. Shen, W. Feng, F. Y. Li, ACS Appl. Mater. Interfaces 2017, 9, 26674; g) D. Ananias, F. A. A. Paz, L. D. Carlos, J. Rocha, Nanoscale 2013, 5, 3079; h) E. N. Ceron, D. H. Ortgies, B. del Rosal, A. Perez-Delgado, K. Santacruz-Gomez, J. Alloys Compd. 2015, 63, 311; i) A. A. S. d. Gama, F. A. A. Paz, B. del Rosal, A. Perez-Delgado, K. Santacruz-Gomez, J. Alloys Compd. 2015, 63, 311; j) A. A. S. d. Gama, F. A. A. Paz, B. del Rosal, A. Perez-Delgado, K. Santacruz-Gomez, J. Alloys Compd. 2015, 63, 311.