Introduction

Currently, the optical thermometric technique based on the fluorescence intensity ratio (FIR) in a phosphor material is attracting intensive investigations, for its advantages such as non-contact, rapid response, and high spatial/temperature resolutions that facilitate temperature detecting for harsh environments or fast moving objects. Most of the previous thermometric material studies focus on the thermally coupled level-pairs (TCL) of rare earth ions (for example, $^{2}H_{11/2}$, $^{4}S_{3/2}$ levels of $\text{Nd}^{3+}$). Indeed, all the reported comparable to this value. The energy separation of the two thermally linked levels of rare-earth ions is less than $2878/7^2$, as reported previously from diverse systems. In this work, we demonstrate that ultrahigh-sensitive temperature sensing can be achieved from Pr$^{3+}$-doped (Ba$_0.7$Sr$_0.3$TiO$_3$) based on the intensity ratio of the $^{1}D_{2}^{2}$-$^{3}H_{4}$ emission to the $^{3}P_{0}^{2}$-$^{3}H_{4}$ emission. The ratio can be increased as much as 90-fold when the temperature rises from room temperature to 513 K, nicely fitting a thermally linked-levels like equation and showing an ultrahigh sensitivity of $4275.1/7^2$. The striking change of the ratio is attributed to the interaction between the two emission levels and the intercalage charge transfer state. This work may have provided a distinct route in the field of optical temperature sensing utilizing rare-earth-doped materials. In addition, the resultant product also possesses excellent photoluminescence and ferroelectric properties, showing promising potentials in multifunctional devices for practical applications.
emission intensity and the $^3D_2 - ^3H_4 / ^3P_0 - ^3H_4$ intensity ratio. Based on these researches, a novel temperature sensing strategy that utilizes the IVCT state interfered Pr$^{3+}$ luminescence to perform optical thermometry is proposed. As an important member of ferroelectric materials, studies of (Ba, Sr)TiO$_3$ materials have been a widely welcomed topic due to their high permittivity, low dielectric loss, high tunability coefficient, quick reaction velocity, anti-breakdown ability and simple fabrication process, etc. Meanwhile, among many advantages is the fact that the (Ba, Sr)TiO$_3$ family is lead-free, and therefore compliant with nowadays requirements for environmentally benign materials. Moreover, (Ba, Sr)TiO$_3$ contains one kind of IVCT (i.e., Pr$^{3+}$–Ti$^{4+}$ IVCT). In this work, we studied the photoluminescence and ferroelectric properties of Pr$^{3+}$ doped Ba$_{0.7}$Sr$_{0.3}$TiO$_3$. The temperature sensor dependence on the fluorescence intensity ratio of the traditional thermally linked $^3P_1 - ^3H_3$ and the $^3P_0 - ^3H_2$ emissions has been studied, which sensitivity is not that significant. Remarkably, FIR of the Pr$^{3+}$–$^3P_0$ and $^1D_2$ emissions exhibits high temperature dependence, the intensity ratio of the $^1D_2 - ^3H_4$ emission to the $^3P_0 - ^3H_4$ emission at 513 K can be increased to as high as 90-fold of that at room temperature, and this temperature-dependent ratio can be nicely fitted by a thermally linked-levels-like equation, strikingly showing an ultrahigh $S$ of 4271.1/$T^2$, which is about 150% of the upper limit of $S$ as introduced above. The configurational coordinate diagram is applied to analyze the mechanism of the temperature-dependent luminescent characteristics, and thermo-induced relaxation between the Pr$^{3+}$–$^3P_0$ and $^1D_2$ levels through the IVCT state is further demonstrated to be the primary cause for the temperature sensing performance of Pr$^{3+}$-doped Ba$_{0.7}$Sr$_{0.3}$TiO$_3$. Meanwhile, it is revealed that doping with Pr$^{3+}$ can further promote the ferroelectric performance of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$. Integrating with the excellent PL and ferroelectric properties, the ultra-high sensitivity on temperature sensing of Pr$^{3+}$-doped Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ not only indicates its remarkable potentials in multifunctional devices, but also may have opened up a distinct and fresh route in the field of highly sensitive optical temperature sensing utilizing rare-earth-doped materials.

### Experimental

Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST) and Ba$_{0.7}$Sr$_{0.295}$Pr$_{0.005}$TiO$_3$ (BST:Pr$^{3+}$) nanoparticles were synthesized by a hydrothermal method. Firstly, 40 ml aqueous solution of strontium nitrates and barium nitrates (1.119375 mol L$^{-1}$, 99%, Aladdin) and praseodymium nitrates (0.005625 mol L$^{-1}$, 99%, Aladdin) were mixed with 23 ml ethanol solution of tetrabutyl titanate (1.25 mol L$^{-1}$, 99%, Aladdin). The pH value of the mixed solution was adjusted to be 13.5 by adding NaOH. The reactive solution was then sealed in a Teflon autoclave at 200 °C for 48 h. After cooling down to room temperature, the obtained product was thoroughly washed by deionized water and ethanol, eventually dried overnight in air.

The crystallization nature and morphology of the samples were characterized using powder X-ray diffraction (Rigaku D/MAX-2600/PC with Cu Kα radiation) and scanning electron microscopy (SEM; JEOL 6700F). Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were measured using a spectrophotometer (HORIBA, Fluoromax-4). The polarization vs. field ($P$–$E$) hysteresis loop was obtained at 50 Hz using a Precision Premier II tester (Radiant Technology USA) at room temperature (30 kV cm$^{-1}$).

### Results and discussion

Fig. 1 present XRD patterns of BST and BST:Pr$^{3+}$ samples. All the peaks in the spectra can be assigned to the BST host structure (PDF#89-0274), and no phases related to impurities were observed. A SEM image of the as-prepared BST:Pr$^{3+}$ sample is shown in the inset of Fig. 1. The average size of these particles is 29,30 μm, which is about 150% of the upper limit of $S$ as introduced above. The configurational coordinate diagram is applied to analyze the mechanism of the temperature-dependent luminescent characteristics, and thermo-induced relaxation between the Pr$^{3+}$–$^3P_0$ and $^1D_2$ levels through the IVCT state is further demonstrated to be the primary cause for the temperature sensing performance of Pr$^{3+}$-doped Ba$_{0.7}$Sr$_{0.3}$TiO$_3$. Meanwhile, it is revealed that doping with Pr$^{3+}$ can further promote the ferroelectric performance of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$. Integrating with the excellent PL and ferroelectric properties, the ultra-high sensitivity on temperature sensing of Pr$^{3+}$-doped Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ not only indicates its remarkable potentials in multifunctional devices, but also may have opened up a distinct and fresh route in the field of highly sensitive optical temperature sensing utilizing rare-earth-doped materials.

**Fig. 1** XRD patterns of BST and BST:Pr$^{3+}$ nanoparticles. SEM image of the BST:Pr$^{3+}$ nanoparticles is presented in the inset.

**Fig. 2** PL spectrum of the BST:Pr$^{3+}$ nanoparticles with an excitation of 325 nm and its PLE spectra monitored at 490 nm and 602 nm.
about 60 nm. All these nanoparticles of BST and BST:Pr3+ samples appear quasi-spherical morphology with a similar size.

According to the PL of BST and BST:Pr3+ (ESI Fig. S1†), the intrinsic BST almost have no PL properties relative to BST:Pr3+, it can be inferred that the PL of BST:Pr3+ is derived from Pr3+. Fig. 2 shows PL and PLE spectra of BST:Pr3+ samples normalized by their maximum intensity. Under 325 nm excitation, the PL spectrum showed a strong blue-green emission at 490 nm corresponding to 3P0−3H5, a strong red emission at 602 nm (3P1−3H4), together with two weak green emissions at 530 nm (3P1−3H6) and 547 nm (3P0−3H6) and two weak red emissions at 617 nm (3P0−3H6) and 651 nm (3P0−3F2). The PLE spectra monitored at 490 nm and 602 nm were exhibit a broad bands centered at 392 nm, which can be attributed to the BST host absorption and the IVCT absorption.33,34 Besides, the sharp peak at 450 nm is ascribed to 3H4 → 1P2 transition of Pr3+.

The variation of emissions of BST:Pr3+ with the temperature over the 290 to 513 K is depicted in Fig. 3, it can be observed that the peak positions of these emission bands are hardly changed and the absolute intensities decrease gradually with temperature. The relative emission intensities for 531 and 547 nm, 490 and 602 nm emissions respond differently to the change of temperature. The intensity of two peaks corresponding to 531 nm (3P1−3H4) and 547 nm (3P0−3H6) transitions at different temperatures are shown in Fig. 4(a). It is obvious from Fig. 4(a) that the intensity of the peak 3P1−3H4 decreases more rapidly compared to 3P0−3H6 due to the thermal agitation. The 3P1 and 3P0 states of Pr3+ are closely spaced with a separation of about 550 cm−1, which belong to TCL.35 As a result, the FIR for the emissions from TCL of Pr3+ ions can be described as:34,35

\[
\text{FIR} = \frac{I_{531}}{I_{547}} = \frac{c_1(r_1)A_1g_1h\nu_1\beta_1}{c_2(r_2)A_2g_2h\nu_2\beta_2}\exp\left(-\frac{(E_1 - E_2)}{kT}\right)
\]

where the emission intensities for the 531 and 547 nm are \(I_{531}\) and \(I_{547}\), respectively. The values of \(c_1(r_1)\) are related to the response of the detection system. \(A_1, g_1, \nu_1\) and \(\beta_1\) are the spontaneous radiative rates, the degeneracy, the photon energy and the branching ratio, respectively, for transitions from the excited 3P1 and 3P0 levels to 3H5 state. \(B\) is a constant; \(\Delta E_{12}\) is the effective energy difference between the 3P1 to 3P0 state; \(k\) is the Boltzmann constant; and \(T\) is the absolute temperature.

The temperature dependence of these emissions at 531 and 547 nm in the range of 290–403 K (Fig. 4(b)) show clear rise in FIR value with temperature, reaching a maximum value when the temperature approaches the maximal experimental temperature 403 K. From a curve fitting of the experimental data, the fitted constants \(B\) and \(\Delta E_{12}\) are 21.25 and 518 cm−1. The fitted \(\Delta E_1\) is close to the experimental value 550 cm−1. To further understand the temperature response of the BST:Pr3+, it is important to investigate the sensing sensitivity, this can be defined from:

\[
S = \frac{\partial R}{\partial T} = R\left(-\frac{\Delta E_{12}}{kT^2}\right)
\]

The sensitivity as a function of temperature (Fig. 4(c)) is 745.2/T² and reach its maximum value of 0.015 K−1 at 375 K in
the temperature range of interest, this phenomenon consist with other groups.\textsuperscript{20,28} It can found that, the PL spectrum of 531 nm and 547 nm emissions is overlap, the precise intensity reading is not very convenient. And due to the rather small energy separation of the \(^3\)P\(_1\) to \(^3\)P\(_0\) state, only \(^3\)S\(_2\) as low as 745.2/T\(^2\) was obtained. So the thermally linked \(^1\)D\(_2\)–\(^3\)H\(_4\) and the \(^3\)P\(_0\)–\(^3\)H\(_5\) emissions are not suitable for the modern development of high performance temperature detection.

Revealed by PL spectra normalized by the \(^1\)D\(_2\)–\(^3\)H\(_4\) emission intensity (refer to Fig. 5(a)), the intensity of all the \(^3\)P\(_0\)-related emissions was reduced much faster than that of the \(^1\)D\(_2\)–\(^3\)H\(_4\) emission upon the temperature rise. Fig. 5(b) presents the calculated intensity ratio of the \(^1\)D\(_2\)–\(^3\)H\(_4\) emission to the \(^3\)P\(_0\)–\(^3\)H\(_5\) emission by referring the maximum emission intensity at 602 nm and 490 nm in the PL spectra, as a function of temperature in the range of 293–513 K. Excitingly, a huge increase as high as 90 fold of the ratio was achieved when the temperature increased from room temperature to 513 K. The intensity ratio can be fit nicely with a thermally linked-levels-like equation, deducing an ultrahigh sensitivity of 4275.1/T\(^2\), which is not only ~6 times higher than that of the optical sensors based on thermally linked \(^3\)P\(_1\) and \(^3\)P\(_0\) levels of Pr\(^{3+}\), but also much higher than all the reported optical sensors based on the fluorescence intensity ratio of rare-earth materials\textsuperscript{8,9,13,29,34,39,40} (as listed in Table 1), where the highest sensitivity of 2878/T\(^2\) was anticipated. The sensitivity keeps increasing in our experimental temperature range and reaches the maximum value 1.055 K\(^{-1}\) at 513 K as shown in Fig. 5(c).

Given that the energy separation between \(^3\)P\(_0\) and \(^1\)D\(_2\) (~4000 cm\(^{-1}\)) is apparently too large to promote the multi-phonon relaxation between the two states, a new viewing angle is, therefore, required to understand the intensity ratio of the two emissions. Interestingly, it has been suggested that, there is a host-dependent IVCT state in Pr\(^{3+}\) doped titanates.\textsuperscript{36–38} In our present work, we demonstrate the IVCT state can interfere with the excited states of Pr\(^{3+}\) including the \(^3\)P\(_0\) level and the \(^1\)D\(_2\) level, and induce the reduction of the Pr\(^{3+}\) emissions or/and provide a de-excitation pathway from the \(^3\)P\(_0\) level to the \(^1\)D\(_2\) state. For a clear illustration for this distinct phenomenon, we depict interactions between the IVCT state and Pr\(^{3+}\) ions in Fig. 6. Under 325 nm excitation, the electron in the valance band is transferred to the conduction band. After fast non-radiative relaxation, the electrons in conduction band relax to the IVCT and the \(^3\)P\(_0\) states simultaneously with different non-radiative rates. The electrons in IVCT state returns to the minimum potential energy position and rapidly transfers to the \(^3\)P\(_0\) and \(^1\)D\(_2\) state with the assistance of thermal phonons. Then we can obtain the blue and red light under 325 nm excitation as shown in Fig. 2. With the rising of temperature, electrons in \(^3\)P\(_0\) state not only transfer to \(^3\)H\(_4\) state, but also transfer to IVCT state by absorbs thermal energy. Then, these electrons in IVCT state relax to \(^1\)D\(_2\) level, which induce the electrons in \(^1\)D\(_2\) state increases relative to \(^3\)P\(_0\) state with the temperature raises, and the intensity ratio of \(^1\)D\(_2\)–\(^3\)H\(_4\)/\(^3\)P\(_0\)–\(^3\)H\(_5\) increases constantly. From the above, it can conclude that thermo-induced relaxation from the \(^3\)P\(_0\) to \(^1\)D\(_2\) level through the IVCT state is the primary cause for the high temperature-dependent FIR in BST:Pr\(^{3+}\).

<table>
<thead>
<tr>
<th>Rare-earth ion (host)</th>
<th>Transition</th>
<th>Sensitivity (K(^{-1}))</th>
<th>Temperature range (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr(^{3+}) (BaSrTiO(_3))</td>
<td>(^3)P(_0)–(^1)D(_2) → (^3)H(_4)</td>
<td>4275.1/T(^2)</td>
<td>290–513</td>
<td>This work</td>
</tr>
<tr>
<td>Pr(^{3+}) (BaSrTiO(_3))</td>
<td>(^3)P(_0)–(^1)D(_2) → (^3)H(_5)</td>
<td>745.2/T(^2)</td>
<td>290–403</td>
<td>This work</td>
</tr>
<tr>
<td>Er(^{3+}) (BaTiO(_3))</td>
<td>(^4)I(<em>{15/2})–(^4)I(</em>{11/2}) → (^4)I(_{5/2})</td>
<td>1026.8/T(^2)</td>
<td>294–923</td>
<td>8</td>
</tr>
<tr>
<td>Nd(^{3+}) (oxylfluoride glass ceramic)</td>
<td>(^4)F(<em>{7/2})–(^4)F(</em>{9/2}) → (^4)I(_{15/2})</td>
<td>3010.1/T(^2)</td>
<td>303–623</td>
<td>9</td>
</tr>
<tr>
<td>Tm(^{3+}) (NaYbF(_4))</td>
<td>(^4)I(<em>{13/2})–(^4)F(</em>{5/2}) → (^4)I(_{15/2})</td>
<td>2007.0/T(^2)</td>
<td>323–773</td>
<td>13</td>
</tr>
<tr>
<td>Pr(^{3+}) (tellurite glass)</td>
<td>(^4)I(<em>{15/2})–(^4)I(</em>{11/2})</td>
<td>879.9/T(^2)</td>
<td>293–473</td>
<td>34</td>
</tr>
<tr>
<td>Pr(^{3+}) (β-NaYF(_4))</td>
<td>(^3)P(_0)–(^1)D(_2)</td>
<td>675.7/T(^2)</td>
<td>120–300</td>
<td>39</td>
</tr>
<tr>
<td>Dy(^{3+}) (Y(_2)Al(_2)O(_3) crystal)</td>
<td>(^4)I(<em>{15/2})–(^4)F(</em>{9/2}) → (^4)H(_{13/2})</td>
<td>1790.4/T(^2)</td>
<td>296–973</td>
<td>39</td>
</tr>
<tr>
<td>Ho(^{3+}) (BaTiO(<em>3)-(Na(</em>{0.5})Ho(_{0.5}))TiO(_3))</td>
<td>(^4)F(<em>{9/2})–(^4)I(</em>{15/2})</td>
<td>933.8/T(^2)</td>
<td>80–600</td>
<td>40</td>
</tr>
</tbody>
</table>
be due to the Pr$^{3+}$ substitution can increase the number of domains contribute to Pr for BST:Pr$^{3+}$. And that a larger orientation and growth of the domains. And that a larger

walls. During the testing process, the stress in the domain walls on the equilibrium and the interaction of between the defects and domain

on the electric remnant polarization of the samples changed from 1.89 to 3.79 domain and the movement of non-180° switchable domain by applied

electric field ($E_c$) of BST:0.5%Pr$^{3+}$ may leads the

which could reach the maximum value 1.055 K−1 at 513 K. Instead of multiphonon relaxation between two thermally coupled states, the big variation of the intensity ratio of the $^1D_2$-$^1H_4$ emission to the $^3P_0$-$^3H_4$ emission upon temperature rise is closely relevant to their interaction with the IVCT state. The ultrahigh sensitivity based on the two emissions may shed a bright light on the promotion of optical temperature sensing and understanding of the involved mechanism. Moreover, the ferroelectric exhibits excellent ferroelectric properties.

Conclusions
In summary, BST:Pr$^{3+}$ ferroelectric samples were prepared by a hydrothermal method. The green emissions at 531 nm and 547 nm were investigated under 325 nm optical excitation in a temperature range from 290 K to 403 K. This investigation revealed that the value of the FIR for $I_{531}/I_{547}$ increases gradually with increasing temperature, and a maximum sensitivity for the BST:Pr$^{3+}$ ceramic of 0.015 K$^{-1}$ at 375 K was reached. Furthermore, BST:Pr$^{3+}$ operated a high sensitivity optical temperature sensor based on $I_{900}/I_{600}$ with a temperature range of 290–513 K, which could reach the maximum value 1.055 K$^{-1}$ at 513 K. The ultrahigh sensitivity based on the two emissions may shed a bright light on the promotion of optical temperature sensing and understanding of the involved mechanism. Moreover, the ferroelectric exhibits excellent ferroelectric properties.

Conflicts of interest
There are no conflicts to declare.

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Notes and references

Although the mechanism deserves further investigation, the ultrahigh sensitivity based on the ratio of $^1D_2$-$^1H_4$ and $^3P_0$-$^3H_4$ emissions may have provided a fresh and favourable route for optical temperature sensing.

Fig. 6 Illustration of the temperature sensing mechanisms of the BST:Pr$^{3+}$ nanoparticles.

Fig. 7 Polarization–electric field hysteresis loops of the BST and BST:Pr$^{3+}$ samples.
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