An upconversion luminescence and temperature sensor based on Yb\textsuperscript{3+}/Er\textsuperscript{3+} co-doped GdSr\textsubscript{2}AlO\textsubscript{5}\textsuperscript{†}

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GdSr\textsubscript{2}AlO\textsubscript{5}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} micro-particles were synthesized by a simple solid state method. The structure, morphology, size and upconversion luminescence features have been characterized. These results indicated that GdSr\textsubscript{2}AlO\textsubscript{5} has a contracted tetragonal cell and has irregular block shaped particles with sizes of about 5 \textmu m. During upconversion, green (\textit{^2}H\textsubscript{11/2}, \textit{^4}S\textsubscript{3/2} \rightarrow \textit{^4}I\textsubscript{15/2}) (527 nm, 549 nm) and red (\textit{^4}F\textsubscript{9/2} \rightarrow \textit{^4}I\textsubscript{15/2}) (665 nm) emissions had been observed, both of which occurred via a two-photon population process. In addition, green UC emission characteristics were studied, and it was found that its temperature ranged from 293 K to 473 K and the sensitivity was 0.0054 K\textsuperscript{–1} at 473 K. This indicated that GdSr\textsubscript{2}AlO\textsubscript{5}:Yb\textsuperscript{3+}/Er\textsuperscript{3+} micro-particles may have potential application in high temperature environments for safety signs.

Temperature-sensitive luminescence materials can provide a non-contact measurement to detect the temperature by probing the dependence of emission intensities on temperature.\textsuperscript{14} We can make the calibration by analyzing the changes on the relative emission intensities when the temperature of the samples increase. The measurement conditions and time exposure can be simple and convenient by this fluorescence intensity ratio (FIR) technique compared with common temperature monitoring devices.\textsuperscript{15–17} The premise of using this method is two thermally coupled levels of RE\textsuperscript{3+} ions. Fortunately the Er\textsuperscript{3+} ions have two thermally coupled energy levels, \textit{^4}H\textsubscript{11/2} and \textit{^4}S\textsubscript{3/2}, with a small energy gap around 770 cm\textsuperscript{–1} which is just conform to this technique.

Host materials play an important role for the UC luminescence. For purpose of obtaining efficient UC emission, lower phonon energies host materials are required because the value of nonradiative decay rates in these hosts would be minimum.\textsuperscript{18,19} Thence, rare earth doped fluoride crystals have been studied for a long time due to their low phonon thresholds. However, it is known to all that physical properties of fluoride crystals could not compared with oxide hosts such as chemical stability and mechanical strength. For this reason, it is still important to find new oxide host materials with efficient UC luminescence. Recently, some literatures on the UC luminescence of RE-doped oxide crystals such as Y\textsubscript{2}O\textsubscript{3}S, SrWO\textsubscript{4}, CaWO\textsubscript{4} and Zn\textsubscript{2}Ga\textsubscript{4}GeO\textsubscript{13} have been reported.\textsuperscript{21,22} Many compounds with Gd ions have been reported due to its excellent magnetic properties. And it is possible to use these compounds as multifunctional materials in various fields. There is little difference in radius of the Yb and Er ions compared with the Gd ions. So rare earth ions as luminescence centers are more easily incorporated into the host, resulting in effective emission. Moreover, aluminate phosphors have been studied extensively by virtue of their cheap raw materials, good chemical and physical stability. In a word, the Yb and Er ions can...
easily doped in the GdSr2AlO5 host and the as prepared GdSr2AlO5 samples are stable enough to work in high temperature and the good magnetic properties would be significant and meaningful for the potential application in biomedical imaging. The structural and optical properties of the Ce3+ doped solid solutions GdSr2AlO5 and Sr2AlO4F are reported by Won Bin Im et al. Lately, yellow emitting phosphor GdSr2AlO5:Ce3+ and afterglow phosphors GdSr2AlO5:RE3+ (RE3+ = Eu3+, Sm3+, Pr3+ and Dy3+) have been investigated as well. These facts illustrated that the GdSr2AlO5 host is a favorable optical material, but there is no report on its UC luminescence. So based on these above points, in our work, the GdSr2AlO5 was studied as a new UC host.

In this paper, Yb3+/Er3+ co-doped GdSr2AlO5 were prepared, Yb3+ were added as the sensitizers with Er3+ as the activators due to the efficient energy transfer from Yb3+ to Er3+. Bright UC emissions from the samples can be seen under 980 nm diode laser excitation. Additionally, the possible mechanism of Yb3+ sensitization to Er3+ on tuning of the UC emission properties were discussed and concluded. The thermometry properties based on the green UC emissions of Er3+ were investigated in detail as well.

2. Experimental

2.1. Synthesis

GdSr2AlO5:RE3+ (RE3+ = Yb3+ and Er3+) samples were synthesized by a simple high temperature solid state reaction method. Raw materials Gd2O3 (99.9%), SrCO3 (99.9%), Al(NO3)3·9H2O (99.0%) and RE oxides (Yb2O3 and Er2O3 99.9%) were weighed out according to the stoichiometric ratio. A mixture was prepared sample has a tetragonal crystal structure, which is the same as the XRD result. The test conditions are 30 kV and 15 mA with a scanning step of 0.02° in the 2θ range from 10° to 80°. The morphologies of the prepared samples were inspected by a thermal field emission scanning electron microscopy (FESEM, TESCAN, MIRA3 XMU). The UC luminescence spectra were measured by using a 980 nm laser diode as the excitation source, with the HORIBA Jobin Yvon Fluorolog-3 Spectro fluorometer system.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the Rietveld structural refinement of the XRD pattern of the GdSr2AlO5 host obtained using the MS program based on the reported tetragonal EuSr2AlO5 in JCPDS card with no.70-2197. The black crosses, red line and green line are corresponds to the calculated pattern, experimental pattern and background, respectively. The violet short vertical lines show the positions of the Bragg reflections of the calculated pattern. The difference between the experimental and calculated patterns is plotted by the blue line at the bottom. The sample can be found to crystallize in the tetragonal space group I4/m m (no. 140). The refinement finally converged to $\chi^2 = 1.686$, $R_{wp} = 7.79\%$ and $R_p = 6.29\%$, indicating that our prepared samples is single phase because all the observed peaks suit the reflection conditions. Furthermore, the lattice constants of GdSr2AlO5:6%Yb3+/1%Er3+ are $a = b = 6.70508\text{Å}$ (ref. 12) $c = 10.90337\text{Å}$ (ref. 22) $\alpha = \gamma = \beta = 90°$.

Fig. 2 presents the TEM, elemental mapping, HRTEM and FFT images of GdSr2AlO5 host. The mapping images indicate a homogeneous distribution of Gd, Sr, Al and O. The HRTEM image exhibits a clear lattice fringe with lattice interplanar spacings of 3.19 Å, corresponding to the (021) plane of GdSr2AlO5. The HRTEM and FFT images demonstrate that the as prepared sample has a tetragonal crystal structure, which is the same as the XRD result.

As a typical sample the SEM image of the GdSr2AlO5:6%Yb3+/1%Er3+ is shown in Fig. 3. It can be find that some of these particles were reunited and the grains have irregular blocky particle shapes with sizes around 5 μm. And the SEM image of

![Fig. 1 XRD refinement results for the GdSr2AlO5 host.](image1)

![Fig. 2 TEM (a), mapping (b), HRTEM and FFT images (c) of GdSr2AlO5 host.](image2)
the GdSr2AlO5 host is show in Fig. S1,† which is almost the same as Fig. 3.

Fig. 4 shows the XRD patterns of various RE ion-doped GdSr2AlO5 samples as well as the experimental and calculated XRD patterns of the GdSr2AlO5 host according to the refinement results. It is clear that the XRD profiles are well fitted with the calculated XRD pattern, and all these diffraction peaks of these phosphors can be accurately assigned to the GdSr2AlO5 host. It can be seen that when the Yb3+ content increased from 0 to 10%, the phase is still the same as GdSr2AlO5 host. So the introduction of lanthanide ions (Yb3+ and Er3+) would not change the phase structure of GdSr2AlO5 except when the Yb3+ doping concentration is 20%. The change of the phase structure means new phase appears with the substantial increase of Yb3+. This phenomenon implies the successful incorporation of Yb ions into the GdSr2AlO5 host.

Furthermore, the experimental values of Gd:Sr:Al:Yb in the as-synthesized 1, 2, 3, 4, 5 and 6 samples are determined by ICP-AES (Table 1), which are all close to the theoretical values.

3.2. UC emission properties

UC luminescence spectroscopy was used to investigate the UC properties of the GdSr2AlO5: Yb, Er under 980 nm laser excitation. It can been seen from Fig. 5 that two UC emissions lied in 527 nm and 549 nm, which were assigned to 2H11/2 → 4I15/2 (Er3+) and 4S3/2 → 4I15/2 (Er3+) transitions, respectively.26 Meanwhile, the red UC emission line centered at 665 nm is observed, which comes from the transition of 4F9/2 → 4I15/2 (Er3+). As the Yb3+ doping concentration increased from 0 to 10%, the UC emission first rapidly increased and then decreased, when the Yb3+ doping concentration reach 6% we get the best emission.

Generally speaking, the absorption can be improved by increasing the doping concentration of the lanthanide ions in the material. But non-radiative multi-phonon relaxation can occur, and the process of cross-relaxation severely limits the range of useful dopant concentrations. Non-radiative multi-phonon relaxation rate between energy levels is another important factor that dictates the population of intermediate and emitting levels and subsequently determines the efficiency of the upconversion process. Therefore, when Yb3+ was co-doped into the lattice in high concentrations, the upconversion luminescence intensity decreased. It can been find that an elevated amount of Yb3+ content is likely to enhance the luminescence efficiency of UC as the Yb3+ ion has a sufficient absorption cross-section matched to common 980 nm laser excitation. Thereby, successive energy transfer processes from Yb3+ to Er3+ play an important role in promoting the Er3+ ion on the ground state to the excited state.27

Additional, we added the upconversion luminescence spectra of Yb and Er doped samples in order to prove the existence of the energy transfer between Yb and Er. From Fig. S2† we can find that the intensity for the upconversion luminescence of Yb, Er co-doped sample is much higher than the singly doped samples. This can be the evidence of the energy transfer between Yb and Er.

These changes of UC luminescence intensity also means the successful incorporation of Yb3+ and Er3+ into the GdSr2AlO5 host. To get a better understanding of the UC luminescence mechanism, the power-dependent UC luminescence properties were studied. In any unsaturated UC process, it is generally considered that the visible emission intensity (Iup) increases regularly according to the pumping power (P) (see Fig. 6). From the UC luminescence spectra of the prepared Yb3+/Er3+ co-doped GdSr2AlO5 under the excitation of a 980 nm diode laser at different pumping powers (100–500 mW cm−2), we can easily find the intensity continued to increase as the pumping power increased.

The relationship between the intensity of UC luminescence Iup and the pump power P can be written as:26–29

\[ I_{up} \propto P^N \]  

where \( N \) is the order of multiphoton transitions, the number of infrared quanta absorbed per photon emission. From the inset in Fig. 5, we can find that the values of \( N \) for sample GdSr2AlO5:6%Yb3+/1%Er3+ are 2.27, 2.07 and 2.13 at 527 nm, 549 nm

Fig. 3 SEM image of GdSr2AlO5: 6% Yb3+ / 1% Er3+.

Fig. 4 XRD patterns of GdSr2AlO5: Yb3+, Er3+.
and 665 nm emissions, indicating 2 photons are needed to realize the transitions of $^2H_{11/2} \rightarrow ^4I_{15/2}$ (527 nm), $^4S_{3/2} \rightarrow ^4I_{15/2}$ (549 nm) and $^4F_{9/2} \rightarrow ^4I_{15/2}$ (665 nm). Yb$^{3+}$ has only two energy levels which match well with specific energy levels of Er$^{3+}$ and it has much bigger absorption cross-section than Er$^{3+}$ when excited with the 980 nm laser.

Fig. 7 shows simplified energy level chart of the Yb$^{3+}$, Er$^{3+}$ as well as the proposed UC mechanisms to produce the multicolor radiation. Since the Yb ions concentration are much higher than Er ions, the most probable UC process is via energy transfer from the Yb ions to Er ions. When excited with laser light at 980 nm, the Yb ions are excited from the $^2F_{7/2}$ level to the $^2F_{5/2}$ level, and then transfer the energies to the nearby Er ions. In Yb$^{3+}$/Er$^{3+}$ co-doped GdSr$_2$AlO$_5$, firstly the Er$^{3+}$ is excited from the $^4I_{13/2}$ ground state to the $^4I_{15/2}$ level and subsequently to the $^4F_{7/2}$ level, and the nonradiative relaxations then populate the states of $^2H_{11/2}$ and $^4S_{3/2}$. Er$^{3+}$ in $^4I_{13/2}$ level are promoted to $^4F_{9/2}$ level by the same energy transfer. Finally, the green emissions at 527 nm and 549 nm are generated by the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions of the Er$^{3+}$, and the red emission centered at 665 nm is due to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ Er$^{3+}$ transition of the Er$^{3+}$.

### 3.3. Temperature sensing properties

Fig. 8a shows the green UC emission spectra of Er$^{3+}$/Yb$^{3+}$ co-doped GdSr$_2$AlO$_5$ in the wavelength range of 500–600 nm at the measured temperatures of 293 K and 473 K. When the temperature increases, we can find the positions of the two green UC emission bands did not change. However, the $R(I_{527}/ I_{549})$ of the two emissions bands varies at different temperature. When the temperature is 293 K, the emission intensity of the $^2H_{11/2} \rightarrow ^4I_{15/2}$ band (527 nm) is lower than $^4S_{3/2} \rightarrow ^4I_{15/2}$ (549 nm) but inverts at a higher temperature (473 K). The relative populations of the two thermally coupled levels, $^2H_{11/2}$ and $^4S_{3/2}$, follows a Boltzmann law, which leads to the variations in the intensities of the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions of the Er$^{3+}$ ions at an raising temperature.

The emission intensity ratio $R$ of the two thermally coupled Er$^{3+}$ energy levels can be defined as:

$$ R = \frac{I_{527}}{I_{549}} = C \exp(-\Delta E/kT) \quad (2) $$

where $I_{527}$ and $I_{549}$ are the integrated intensities from the $^{2}H_{11/2}$ $\rightarrow$ $^{4}I_{15/2}$ and $^{4}S_{3/2}$ $\rightarrow$ $^{4}I_{15/2}$ transitions of Er$^{3+}$, respectively, $\Delta E$ is the energy separation between the $^{2}H_{11/2}$ and $^{4}S_{3/2}$ levels, $k$ is the

### Table 1: Ions content in GdSr$_2$AlO$_5$ samples by ICP-AES

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
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<tr>
<td>Gd</td>
<td>0.99</td>
<td>0.97</td>
<td>0.94</td>
<td>0.93</td>
<td>0.92</td>
<td>0.89</td>
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<tr>
<td>Sr</td>
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<td>0.90009</td>
<td>0.88310</td>
<td>0.96490</td>
<td>0.95768</td>
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<tr>
<td>Al</td>
<td>2</td>
<td>2</td>
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<td>2</td>
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</tr>
<tr>
<td>Yb</td>
<td>1.01010</td>
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<td>1.05427</td>
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<td>0.01</td>
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<tr>
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<td>0.01067</td>
<td>0.01109</td>
<td>0.01010</td>
<td>0.01001</td>
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</tbody>
</table>

Fig. 5 UC spectra of GdSr$_2$AlO$_5$:Yb$^{3+}$,1%Er$^{3+}$ crystals with different Yb$^{3+}$ doping conditions under the excitation of 980 nm laser.

Fig. 6 UC spectra of GdSr$_2$AlO$_5$:6%Yb$^{3+}$/1%Er$^{3+}$ and (inset) Ln–Ln plot of emission intensity of different excited states versus excitation power of GdSr$_2$AlO$_5$:6%Yb$^{3+}$/1%Er$^{3+}$. 

Note: This page contains a table with ions content in GdSr$_2$AlO$_5$ samples by ICP-AES. The table shows the theoretical and experimental content for Gd, Sr, Al, Yb, and Er ions in samples labeled 1 to 6.
Boltzmann constant and \( T \) is the temperature (in K). Fig. 8b shows the change of the \( R \) for the emission bands centered at 527 nm and 549 nm as a function of the inverse absolute temperature on a monolog scale. The linear behavior of the curve shows the applicability of the material for temperature sensing applications.\(^{34}\) The \( \ln R \) as a function of \( 1/T \) is perfectly fitted to a linear equation with the slope of \(-1189.2\) and use the eqn (2) the \( C \) can be calculated. Thus, the expression of \( R \) could be determined as \( R = 12.395 \exp(-1189.2/T) \) (see Fig. 8c). Furthermore, understanding the rate at which the measured temperature-sensitive parameter varies for a certain change in temperature is significance for temperature sensing applications. Hence the sensor sensitivity can be written as:

\[
\text{Sensitivity (S) = dR/dT} = R(-\Delta E/kT^2) \tag{3}
\]

Here the symbols have their usual meanings. The sensor sensitivity was calculated by this equation and it was plotted in Fig. 8d. Impressively, the sensitivity increases gradually as the temperature rise from 293 K to 473 K, and reached the peak at about 0.0054 K\(^{-1}\) at 473 K. The UC emission intensity is quite stable up to the measured temperature at 473 K, which suggests it may be suitable at higher temperatures as well. However as a lack of available devices the research at higher temperature could not be furthered done. Therefore, this study reveals that the GdSr\(_2\)AlO\(_5\) host is a good material for UC-based temperature sensors.

Besides the dependence of the \( R(\text{red}/\text{green})\)ratio on temperature, the effect of temperature on the ratio of red and green emissions (R/G) were also observed. Fig. 9a shows the relationship between temperature and the R/G ratio. Evidently, the R/G ratio tends to decreases with the increase of the temperature. So the emission color of the sample could be changed by controlling the temperature. In order to insight the relationship between emission color of the sample and temperature more clearly, the CIE 1931 coordinates of the prepared GdSr\(_2\)AlO\(_5\):6\% Yb\(^{3+}\),1\%Er\(^{3+}\) micro-particles in the range of temperatures 293–473 K were calculated from the recorded UC luminescence spectra and the corresponding results are shown in the CIE 1931 coordinates diagram in Fig. 9b. It can be seen that the UC emission color can be changed from yellow to green as the rise of temperature, this means a decrease tendency of the emission intensity ratio of red and green emissions can been observed with the increase of temperature. This is the same as the result shows in Fig. 9a.

It is known to all that the nonradiative transition rate of RE\(^{3+}\) ions for multiphonon relaxation can be written by the following equation:\(^{35,36}\)

\[
W_{NR} = W_{NR}(0)\exp(-\Delta E/kT) \tag{4}
\]

where \( W_{NR}(0) \) is the nonradiative relaxation rate at 0 K, \( \Delta E \) is the energy separation between the \(^2\)H\(_{11/2}\) and \(^4\)S\(_{3/2}\) levels (700 cm\(^{-1}\)), \( k \) is Boltzmann’s constant, and \( T \) is the absolute temperature. And then, we can conclude that the nonradiative transition rate will increase as the temperature increases. In Yb\(^{3+}/\text{Er}^{3+}\) co-doped systems, actually, the emission intensities from all the transitions would decreases due to the multiphonon relaxation processes when the temperature increases. This means a significant decline of population on the \(^4\)F\(_{9/2}\) level due to the successively nonradiative processes of \(^4\)F\(_{9/2} \rightarrow ^4\)I\(_{11/2} \rightarrow ^4\)I\(_{13/2} \rightarrow ^4\)I\(_{15/2}\) are dominant at high temperature.

Thereby, both the green and red emission intensities will decrease greatly at higher temperature in normal situation. However, owing to the \(^2\)H\(_{11/2}\) and \(^4\)S\(_{3/2}\) levels are thermally coupled, much more electrons will be excited to the \(^2\)H\(_{11/2}\) level from the \(^4\)S\(_{3/2}\) level at high temperature. The occurrence of this phenomenon would block the de-excited process of the \(^4\)S\(_{3/2}\) level extremely via the nonradiative transition of \(^2\)H\(_{11/2} \rightarrow ^4\)S\(_{3/2} \rightarrow ^4\)F\(_{9/2}\). Thence, the decrease of the total emission intensity of green color would be limited, this lead to the greatly decrease of the ratio of red and green emissions when the temperature arises. The temperature-dependent characteristic of the as-prepared GdSr\(_2\)AlO\(_5\):Yb\(^{3+}\), Er\(^{3+}\) micro-particles means that this host could be also adopted as safety sign in high temperature environment as well as optical thermograph.

![Fig. 7](image_url)

Fig. 7 Implied energy level diagram of Yb\(^{3+}\) and Er\(^{3+}\) and the possible UC mechanism of GdSr\(_2\)AlO\(_5\):6\%Yb\(^{3+}\)/1\%Er\(^{3+}\).
Conflicts of interest

There are no conflicts to declare.

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Notes and references

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