A facile and controllable ethanol/water aided hydrothermal process was developed to prepare the NaCaSiO3OH:Tb3+/Eu3+ phosphor. The morphologies were in situ constructed with the phase transformation from NaCaSiO3OH to Na2Ca2Si2O7, and the intrinsic crystal structural transformation mechanism and the dependence of their photoluminescence tuning on the Tb3+/Eu3+ ratio have been discussed.

The design and synthesis of rare earth (RE) ions doped luminescent materials with controllable morphologies remains a challenge owing to their size/shape-dependent properties and induced potential applications in lighting devices, biological labeling, lasers, displays, etc. The physical-chemical properties of materials could be controlled as we desired through a good manipulation of the size and morphology. Therefore, fabrication of RE doped luminescent materials with controlled structures and morphologies is still one of the challenging issues in chemistry and materials science. Amongst them, RE doped silicate materials have been widely investigated due to the versatility in their crystal structures and tunable luminescence properties, which are suitable for application to many fields. Usually, high-temperature solid-state reactions are employed to prepare silicate materials. So, the resultant samples appear in aggregation with an irregular shape, and such a preparation method limits the possibility of tuning the morphology and the following properties of the final products. Accordingly, various solution-based preparation techniques, such as co-precipitation, hydrothermal, sol-gel, have been explored to prepare silicate materials with controllable morphologies, which is still a challenge.

Herein, we present a facile pathway toward Eu3+/Tb3+ doped Na2Ca2Si2O7 phosphors that rely on the heat treatment of the NaCaSiO3OH:Eu3+/Tb3+ precursor prepared using a controllable hydrothermal method. By tuning the ethanol/water (EtOH/H2O) ratio, it is possible to yield different precursor morphologies, such as rods, decahedron, distorted octahedron and spindle. Then, we synthesized Na2Ca2Si2O7 with the same particle shapes as those of NaCaSiO3OH, as obtained from the in situ construction and phase transformation from NaCaSiO3OH to Na2Ca2Si2O7. Additionally, the luminescence properties of Eu3+/Tb3+ doped NaCaSiO3OH and Na2Ca2Si2O7 microstructures are comparatively investigated, and the luminescent colors of Na2Ca2Si2O7:Tb3+,Eu3+ can be adjusted from red to green depending on the Tb3+/Eu3+ ratio, which should be ascribed to the energy transfer of Tb3+ → Eu3+. The work reveals that our current hydrothermal method following a heat treatment process is a facile and efficient way to the synthesis of such phosphors with controlled morphologies.

The preparation method employed for all the presented materials is described in detail in the ESI. Herein, the X-ray diffraction (XRD) patterns of the NaCaSiO3OH samples prepared by the addition of different EtOH/H2O volume ratios are shown in Fig. 1. From Fig. 1 and Fig. S1a (ESI†), it can be observed that all samples exhibit a single phase and all peaks are assigned to the monoclinic phase NaCaSiO3OH (JCPDS card no. 25-1319). The dependence of the NaCaSiO3OH morphology on the reaction media of the EtOH/H2O volume ratio is illustrated well by the scanning electron microscopic (SEM) evaluation of the isolated products (see Fig. 2 and Fig. S1b, c, ESI†). Rod-like particles are obtained when the volume of H2O is 30 ml (Fig. 2a), and some rods are agglomerated to form rod bunches. From Fig. 2b, the morphology of NaCaSiO3OH is changing progressively to a nubby shape in the presence of 1 ml EtOH. Increasing the EtOH volume to 5 ml (EtOH/H2O = 5/25) yields a perfect decahedron shape noted in Fig. 2c, indicating that the decahedral structure may have grown from rods. Based on the high magnification SEM image (the inset of Fig. 2c), the decahedrons with some rips are highly uniform and symmetrical, and they exhibit a bigger size compared to the sample prepared in EtOH/H2O = 1/29. Upon addition of 10 ml ETOH, the decahedral shape transforms into octahedron one, but the two sides of the selected octahedron are...
The thermal stability of the NaCaSiO$_3$OH phase is firstly investigated by thermogravimetric and differential scanning calorimetry (TG-DSC) analysis. From the recorded TG-DSC results during the heat-treatment of NaCaSiO$_3$OH in air (Fig. 3a), it is apparent that the decomposition starts at 460 °C and finishes at 523 °C with the weight loss of 5.64%, which agrees with the theoretical value (5.76%) calculated from the dehydration of two NaCaSiO$_3$OH molecules. Hence, the phase decomposition is proposed over the temperature range of 450–530 °C. To verify the occurrence of phase transformation and find the exact phase transformation temperature, variable temperature X-ray diffraction (VT-XRD) is employed in situ. As shown in VT-XRD patterns (Fig. 3b), we find that the NaCaSiO$_3$OH phase is thermally stable up to 450 °C in air. At 500 °C, a mixture of the NaCaSiO$_3$OH phase and the newly formed Na$_2$Ca$_2$Si$_2$O$_7$ phase (ICSD card no. 95858) appears. However, all the characteristic XRD peaks coincide with the standard pattern of Na$_2$Ca$_2$Si$_2$O$_7$, when the temperature is increased to 600 °C. Even if the heating temperature rises up to 1000 °C continuously, the Na$_2$Ca$_2$Si$_2$O$_7$ phase still maintained, confirming that the temperature of phase transformation from NaCaSiO$_3$OH to Na$_2$Ca$_2$Si$_2$O$_7$ is about 500 °C, as observed from the TG-DSC results. Fig. 3c shows the SEM images of the resultant Na$_2$Ca$_2$Si$_2$O$_7$. More interestingly, it can be found that the morphologies of NaCaSiO$_3$OH can be kept in situ even if it is sintered at 700 °C to form the Na$_2$Ca$_2$Si$_2$O$_7$ phase. We believe that such a phase transformation synthesis should be a general and facile way to prepare morphology-controllable silicate materials. Moreover, Fig. 3d gives the enlarged image of the individual Na$_2$Ca$_2$Si$_2$O$_7$ particle, and the porous surface character can be observed, which implies the decomposition of NaCaSiO$_3$OH via evaporation of H$_2$O molecular and the appearance of microscopic pores on the surface of the particles. The intrinsic crystal structural transformation mechanism will also be discussed in the following section.

The phase transformation mechanism for the formation of the Na$_2$Ca$_2$Si$_2$O$_7$ phase with microscopic pores on the particle surface was not smooth (the inset of Fig. 2d). Upon further increasing the EtOH to 15 ml, the spindle shape is developed, and the centre thickness of the spindle is greater than the edge thickness. Then, under a rich amount of EtOH (20–30 ml), pure phase NaCaSiO$_3$OH is still formed, but the morphology of NaCaSiO$_3$OH particles become more irregular, even giving rise to crystal aggregates as illustrated in Fig. 2f and Fig. S1b, c (ESI†). More interestingly, it is observed that the higher the EtOH content (5–30 ml), the smaller the particle size. Therefore, we can conclude that the difference of morphologies and sizes in this surfactant/ligand-free system is mainly governed by the amount of the solvent EtOH. Generally, the growth of crystals and the formation of various morphologies are complex processes that are the cooperative results of the inherent structures and the external experimental conditions.\[12-14\] In our case, two kinds of solvents (H$_2$O and EtOH) with different polarities and saturated vapour pressures are used as reaction media, producing a distinguished morphology and a size of NaCaSiO$_3$OH. The polarities and saturated vapour pressures of the solvents were found to affect the products under thermal conditions by giving adjustments to the homogenization of the reactants, the amount of individual nucleus formation, the amalgamation and direction preference of growing nucleus.\[15\] Furthermore, the ratio of two solvents would affect the solubility of the starting materials, the reaction rate and the crystallization rate of products, which result in the various morphologies, as observed in the present and other experiments.\[12-14\]
is proposed in Fig. 4. As we know, both the NaCaSiO$_3$OH and Na$_2$Ca$_2$Si$_2$O$_7$ belong to monoclinic phases, but their space groups are $P2_1/m$ and $C2/c$ respectively and their cell parameters are absolutely distinguished. Therefore, such a phase transformation doesn’t belong to the topotactic transformation because two structures have unit cells without relations. Besides these, other differences of the two structures are manifested as follows: (1) Na$_2$Ca$_2$Si$_2$O$_7$ consists of Ca, Na/Ca, Na and Si sites, but NaCaSiO$_3$OH merely consists of Ca, Na and Si cations, no Ca/Na mixing exists in NaCaSiO$_3$OH; (2) networks of SiO$_4$ polyhedra are different, namely, there are isolated SiO$_4$ in NaCaSiO$_3$OH and two Na$_2$Ca$_2$Si$_2$O$_7$ phase. The expansion of vacancies may lead to the formation of vacancies should be formed during the formation of the new phase. In this case we can suggest that OH groups of two SiO$_3$OH tetrahedra combine with two H ions from other two SiO$_3$OH tetrahedra forming two H$_2$O molecules. The remaining two SiO$_4$ and two SiO$_4$ form Si$_3$O$_{10}$ + SiO$_4$ as illustrated in the bottom panel of Fig. 4. The possible chemical reaction equation of the formation of Na$_2$Ca$_2$Si$_2$O$_7$ from NaCaSiO$_3$OH could be described as follows:

$$\text{NaCaSiO}_3\text{OH} + \text{NaCaSiO}_3\text{OH} \xrightarrow{\text{in air} \text{ at } 700^\circ \text{C}} \text{Na}_2\text{Ca}_2\text{Si}_2\text{O}_7 + \text{H}_2\text{O}$$

In the phase transition process, the dehydration from NaCaSiO$_3$OH results in the generation of H$_2$O then, a large amount of vacancies should be formed during the formation of the new Na$_2$Ca$_2$Si$_2$O$_7$ phase. The expansion of vacancies may lead to the formation of cracks and microscopic pores at the Na$_2$Ca$_2$Si$_2$O$_7$ polyhedron facets. The SEM images of calcined product Na$_2$Ca$_2$Si$_2$O$_7$ [Fig. 3d] show that the polyhedrons possess many microscopic holes, which supports the above proposed mechanism.

Our experiments have also shown that both NaCaSiO$_3$OH and Na$_2$Ca$_2$Si$_2$O$_7$ are good hosts for the luminescent materials formed via the Eu$^{3+}$/Tb$^{3+}$ doping. It should be mentioned that the doping of Eu$^{3+}$/Tb$^{3+}$ into NaCaSiO$_3$OH and Na$_2$Ca$_2$Si$_2$O$_7$ does not change the phase purity and morphology of the final products as displayed in Fig. S3 [ESI†]. Herein, the luminescence properties of Eu$^{3+}$ and Tb$^{3+}$ singly or/and codoped NaCaSiO$_3$OH and Na$_2$Ca$_2$Si$_2$O$_7$ samples with a decahedron-like shape (EtOH/H$_2$O = 5/25) were comparatively investigated. Fig. 5a and b show the photoluminescence (PL) emission spectra of NaCaSiO$_3$OH:0.10Eu$^{3+}$/0.03Tb$^{3+}$ and Na$_2$Ca$_2$Si$_2$O$_7$:0.10Eu$^{3+}$/0.03Tb$^{3+}$ samples, respectively. NaCaSiO$_3$OH:Eu$^{3+}$ shows a strong red luminescence originating from the $^5D_0 \rightarrow ^7F_1$ transitions of Eu$^{3+}$ ions under 254 nm excitation.$^{16,17}$ For the Na$_2$Ca$_2$Si$_2$O$_7$:Eu$^{3+}$ sample, the PL spectrum exclusively contains the characteristic emission of Eu$^{3+}$ centered at 611 nm. On the other hand, NaCaSiO$_3$OH:Tb$^{3+}$ shows a series of strong green emission lines with a maximum at about 542 nm, which are all ascribed to $^5D_4 \rightarrow ^7F_j$ ($j = 6, 5, 4, 3$) transitions of Tb$^{3+}$ corresponding to $^5D_4 \rightarrow ^7F_5$ (488 nm), $^5D_4 \rightarrow ^7F_4$ (542 and 550 nm), $^5D_4 \rightarrow ^7F_3$ (583 nm) and $^5D_4 \rightarrow ^7F_2$ (625 nm), respectively, which are similar to other Tb$^{3+}$-containing phosphors, such as Tb$_2$(MoO$_4$)$_3$.$^{18,19}$ For the Na$_2$Ca$_2$Si$_2$O$_7$:Tb$^{3+}$, the emission spectral lines in the blue region are found to be at 416 nm ($^5D_4 \rightarrow ^7F_2$) and 437 nm ($^5D_4 \rightarrow ^7F_1$) with high emission intensity. However, they do not emerge in the emission spectra of NaCaSiO$_3$OH:Tb$^{3+}$, which means that there is a relatively low photon energy of Na$_2$Ca$_2$Si$_2$O$_7$ compared to that of NaCaSiO$_3$OH. Moreover, the intensity ratio of $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions of Eu$^{3+}$ ions in different hosts is related to the activator symmetry occupied in the lattice. The strong emission from $^5D_0 \rightarrow ^7F_2$ compared to that of $^5D_0 \rightarrow ^7F_1$ in NaCaSiO$_3$OH:0.10Eu$^{3+}$ denotes that there is relatively low symmetry for Na$_2$Ca$_2$Si$_2$O$_7$. Therefore, it is found that there is obvious difference in the emission spectra of NaCaSiO$_3$OH:Eu$^{3+}$ and Na$_2$Ca$_2$Si$_2$O$_7$:Eu$^{3+}$ as well as NaCaSiO$_3$OH:Tb$^{3+}$ and Na$_2$Ca$_2$Si$_2$O$_7$:Tb$^{3+}$. The effects can be attributed to the different coordination environments and symmetry around the Tb$^{3+}$/Eu$^{3+}$ ions in the NaCaSiO$_3$OH and
Na$_2$Ca$_2$Si$_2$O$_7$ hosts.\textsuperscript{12} Furthermore, from Fig. 5c, the spectral overlap between the PL spectrum of Na$_2$Ca$_2$Si$_2$O$_7$:Tb$^{3+}$ and photo-luminescence excitation (PLE) spectrum of Na$_2$Ca$_2$Si$_2$O$_7$:Eu$^{3+}$ can be observed, and the PL spectra of Na$_2$Ca$_2$Si$_2$O$_7$:Tb$^{3+}$, Eu$^{3+}$ consist of the peaks at 611 nm and 542 nm attributed to Eu$^{3+}$ and Tb$^{3+}$, respectively. The results suggest that the energy transfer can occur from Tbz to Eu$^{3+}$,\textsuperscript{20} and the emitting colour can be tuned from green to yellow and red via energy transfer of Tbz$^+\rightarrow$ Eu$^{3+}$ by tuning the doped Eu$^{3+}$ concentrations as shown in Fig. 5d and the inset.

In order to further investigate the energy transfer process between Tbz$^+$ and Eu$^{3+}$, the decay curves of Tbz$^+$ by monitoring the emission transition at 542 nm were measured and depicted in Fig. 6(a). The decay curve can be well fitted with a second-order exponential decay mode by using eqn (1):\textsuperscript{21–23}

\[
I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]  

(1)

where \(I\) is the luminescence intensity, \(A_1\) and \(A_2\) are constants, \(t\) is the time, \(\tau_1\) and \(\tau_2\) are rapid and slow lifetime values for exponential components, respectively. Based on the eqn (1), one can obtain the \(A_1, A_2, \tau_1\) and \(\tau_2\) values by fitting of the decay curves. Therefore, the effective lifetime constant \((\tau^{*})\) can be calculated as eqn (2):

\[
\tau^{*} = \frac{(A_1\tau_1^{-2} + A_2\tau_2^{-2})/(A_1\tau_1 + A_2\tau_2)}{A_1 + A_2}
\]  

(2)

The effective decay time \((\tau^{*})\) was calculated to be 4.01, 3.88, 3.52 and 3.25 ms for Na$_2$Ca$_2$Si$_2$O$_7$:0.03Tb$^{3+}$,Eu$^{3+}$ with \(x = 0, 0.04, 0.08\) and 0.10, respectively. The energy-transfer efficiency \((\eta_T)\) from Tbz$^+$ to Eu$^{3+}$ ions can be expressed as the following eqn (3):\textsuperscript{23–26}

\[
\eta_T = 1 - (I_S/I_0) = 1 - (\tau_S/\tau_0)
\]  

(3)

where \(\tau_S\) and \(\tau_0\) stand for the lifetimes of Tbz$^{3+}$ in the absence and the presence of Eu$^{3+}$ respectively. With the increase in the Eu$^{3+}$ concentration, the \(\eta_T\) value is calculated and the results are shown in Fig. 6(b). As displayed in Fig. 6(b), the average lifetime decreased monotonically and the energy-transfer efficiency increased with the increasing Eu$^{3+}$ content. The \(\eta_T\) value reached a maximum of 19% at \(x = 0.10\).

In summary, we have presented for the first time a simple hydrothermal method for the synthesis of highly crystallized NaCaSiO$_3$OH particles with a controlled morphology/size in the presence of EtOH as both the solvent and the structure-directing agent. More importantly, the as-prepared NaCaSiO$_3$OH can be in situ transferred into Na$_2$Ca$_2$Si$_2$O$_7$ by the heat-treatment in air, and the morphologies of the as-prepared NaCaSiO$_3$OH have been kept without any agglomerations. In principle, this method offers a new alternative strategy to generate silicate materials. Moreover, when Na$_2$Ca$_2$Si$_2$O$_7$ is codoped with Eu$^{3+}$ and Tbz$^{3+}$ with an appropriate ratio, the emission colours of the Na$_2$Ca$_2$Si$_2$O$_7$:Tb$^{3+}$, Eu$^{3+}$ phosphors can be tuned from green to yellow and red. It is expected that the morphology-controlled Na$_2$Ca$_2$Si$_2$O$_7$:Tb$^{3+}$, Eu$^{3+}$ micro-particles will provide potential applications for micro/nano functional devices.

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Notes and references