

# Luminescence properties of double-perovskite $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$ red-emitting phosphors prepared by the citric acid-assisted sol–gel method

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**Abstract** Double-perovskite  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  red-emitting phosphors were prepared by the citric acid-assisted sol–gel method, and their luminescence properties were investigated as a function of sintering temperature and  $\text{Eu}^{3+}$ -doping concentration. B-site substituted  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  phosphor, in which  $\text{Na}^+$  ions act as charge compensators, was selected to study the thermal behavior, phase structure, microstructure, and photoluminescence property under different sintering temperatures. The photoluminescence studies on  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  ( $x = 0.02, 0.05, 0.10, 0.15, 0.2$ ) show that a dominant red emission line at around 594 nm, which is due to the  $\text{Eu}^{3+}$  magnetic dipole transition of  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ , is observed under different  $\text{Eu}^{3+}$  excitations (396 and 412 nm). Further,  $\text{Eu}^{3+}$  dopant content dependent emission spectra investigations of  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  phosphors indicates that, when the  $\text{Eu}^{3+}$  concentrations  $x = 0.05$ , there are minimum differences between the emission intensity of  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$  transition at 594 nm and that of  ${}^5\text{D}_0\text{--}{}^7\text{F}_2$  transition at 615 nm. With increasing  $\text{Eu}^{3+}$  concentration, the variation of the emission intensities between the two transitions keep nearly invariable and  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  phosphor has the strongest red emission in this series.

## Introduction

White light-emitting diodes (w-LEDs) are considered as the next-generation light source because of their high luminous efficiency, long lifetimes, low environmental impact, and small structure type [1, 2]. Among them, phosphor-converted w-LEDs have the enough interests in the industrial and academic fields, and there are two ways to realize the white light emission [3]. One scheme is the combination of the blue LEDs chip and the yellow-emitting phosphor, and the other is the combination of the near ultraviolet (NUV) LEDs chip and the red-, green- and blue-emitting phosphors [4]. For the first scheme, it is based on blue LED plus yellow phosphor, which has low color-rendering index (CRI) because of lack of red component in their spectra [5]. As expected, red-emitting phosphor used to compensate yellow-emitting phosphor is introduced to improve the CRI and increase the light conversion efficiency [6]. Similarly, for the second scheme, NUV light-excitable red-emitting phosphor for w-LEDs is also essential [7]. Hence, there has been a widespread and growing interest in developing new families of red-emitting phosphors with high absorption in the near UV to blue region [8–10].

Tungstate and molybdate are two families as the hosts of phosphors that have promising applications as the red component of w-LEDs, and the incorporation of  $\text{Eu}^{3+}$  into tungstate and molybdate crystal lattice modifies the luminescence spectra due to the formation of the emission centers that generate the specific red light [11–14]. Recently, there are many reported references on novel tungstate and molybdate red-emitting phosphors, such as  $\text{LiEuM}_2\text{O}_8$  ( $M = \text{Mo}, \text{W}$ ) [11],  $\text{R}_{2-x}\text{Eu}_x(\text{MoO}_4)_3$  ( $R = \text{La}, \text{Y}, \text{Gd}$ ) [12],  $(\text{Ca}, \text{Eu}, \text{M})(\text{WO}_4)_{1-z}(\text{MoO}_4)_z$  ( $M = \text{Mg}, \text{Zn}$ ) [13],  $\text{M}_3\text{Eu}(\text{WO}_4)_{4-x}(\text{MoO}_4)_x$  ( $M = \text{Li}, \text{Na}, \text{K}$ ) [14], and

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so on. Among them, a kind of double-perovskites  $A_2CaMoO_6$  ( $A = Sr, Ba; M = Mo, W$ ) used as red component of w-LEDs has attracted many scientists' attentions [15–17]. This is ascribed to that the physical properties of double-perovskites  $AB_{1/2}B'_{1/2}O_3$  are strongly influenced by the degree of B-cation ordering, and then color-tunable luminescence properties can be detected. Thus, we selected  $Sr_2CaMoO_6$  as a potential red-emitting phosphor in this study.

Among the previously reported references, many tungstate and molybdate phosphors were synthesized by conventional solid-state reaction method [11–17]. Therefore, the aggregation and inhomogeneous shape are unavoidable, which inhibit the absorption of the excitation energy and, therefore, reduce the emission intensity. Sol–gel method is one of the most important “soft chemistry” techniques for the synthesis of phosphor materials with higher uniformity in particle size distribution, non-agglomeration and higher photoluminescence intensity [18]. In this article, to the best of our knowledge, we first reported the preparation of double-perovskites  $Sr_2CaMoO_6$  red-emitting phosphors by sol–gel process and their luminescence properties.

## Experimental

Red-emitting phosphors,  $Sr_2Ca_{1-2x}Eu_xNa_xMoO_6$  ( $x = 0.02, 0.05, 0.10, 0.15, 0.2$ ), were prepared by the citric acid-assisted sol–gel method. The starting materials used in the preparation were  $Sr(NO_3)_2 \cdot 6H_2O$  (analytical reagent, A.R.),  $Ca(NO_3)_2 \cdot 6H_2O$  (A.R.),  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  (A.R.),  $Eu_2O_3$  (99.999%),  $Na_2CO_3$  (A.R.),  $HNO_3$  (A.R.), citric acid (A.R.), and deionized water. According to the chemical formulas stated above, stoichiometric amount of  $Eu_2O_3$  was dissolved in dilute  $HNO_3$  (A.R.) under vigorous stirring. Then stoichiometric amount of  $Sr(NO_3)_2 \cdot 6H_2O$ ,  $Ca(NO_3)_2 \cdot 6H_2O$ ,  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ , and a suitable volume of deionized water was added and stirred homogeneously. Citric acid was added to the solution as chelating agent for the metal ions. The molar ratio of total chelate metal cations to citric acid was 1:1.5. At the end, the pH value of the final solution was adjusted to 7, 8 by the addition of suitable amount of dilute  $NH_3 \cdot H_2O$ . Finally, the highly transparent solution was obtained after stirring for a few minutes. Then the transparent solution was heated at 353 K in oven to get transparent light-brown sol, and the sol was further dried at 403 K in oven for 48 h to get dried gel. The dried gel was annealed at 873 K for 12 h in air to get the foamed precursor, and the precursor was further sintered at different temperatures for 8 h in air to get the white phosphor powder.

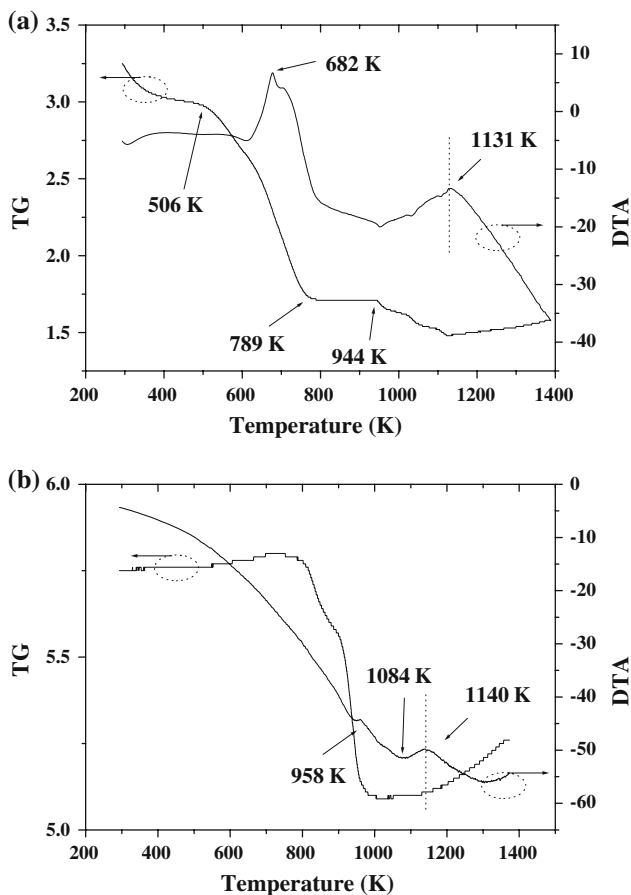
Thermogravimetry–differential thermal analyzer (TG-DTA) for the dried gel and sintered precursor at 873 K were

performed on a SHIMADZU model DTG-60AH TG-DTA instrument. The analyzer was operated at a heat rate of 2 K/min from room temperature to a maximum temperature of 1373 K. The X-ray diffraction (XRD) patterns were recorded by using a SHIMADZU model XRD-6000 X-ray powder diffractometer (Cu  $K\alpha$  radiation, 40 kV, 30 mA, and a scanning speed  $2.0^\circ (2\theta)\text{min}^{-1}$ ). Fourier transform infrared spectroscopy (FT-IR) data were collected on a FTIT-AVATAR370 spectrophotometer over the range of wavenumber  $4000\text{--}400\text{ cm}^{-1}$ , and the standard KBr pellet technique was employed. A scanning electron microscope (SEM, JEOL, JSM-6490) was employed to analyze the size and shape of the selected samples. Diffuse reflection spectra of as-synthesized phosphor powder samples were measured on a UV-Vis-NIR spectrophotometer (UV-3600, SHIMADZU) attached to an integral sphere.  $BaSO_4$  was used as a reference standard. The excitation and emission spectra were recorded by using a Perkin–Elmer LS-55 fluorescence spectrophotometer with a photomultiplier tube operating at 400 V, and a 150 W Xe lamp was used as the excitation lamp. All the measurements for the as-synthesized samples were performed at room temperature.

## Results and discussion

### TG-DTA analysis

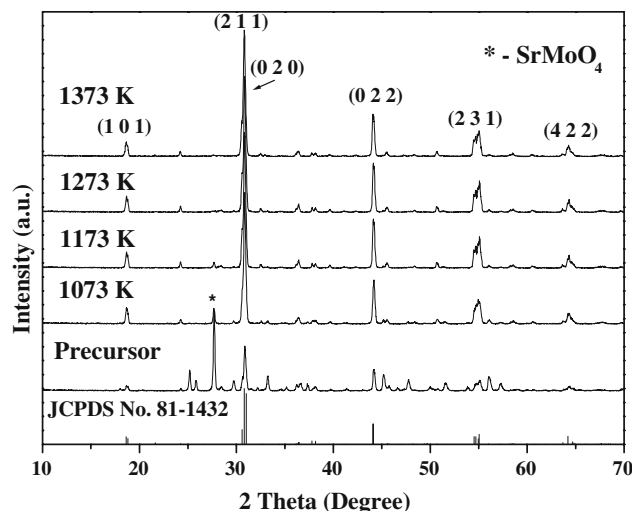
Figure 1 gives the TG-DTA curves of dried gel (a) and sintered precursors at 873 K (b) of  $Sr_2Ca_{0.8}Eu_{0.1}Na_{0.1}MoO_6$ . In order to understand the pyrolysis behavior of the complex dried gel, Fig. 1a indicates that the weight loss of the dried gel occurs in the TG curve from room temperature to 789 K, which also corresponds to a strong endothermic peak at about 682 K in DTA curve. This stage should originate from the decomposition and burning of organic chelate agents. After that, a small exothermic peak at about 944 K is shown in the DTA curve, and it also shows an obvious weight loss in TG curve, which is attributed to the decomposition of metal nitrates in the starting materials. Finally, there is a weak endothermic peak at about 1131 K in DTA curve, but no obvious weight loss can be found in TG curve. Therefore, it indicates that the  $Sr_2Ca_{0.8}Eu_{0.1}Na_{0.1}MoO_6$  phase is formed completely. Further, in Fig. 1b, TG-DTA curves of  $Sr_2Ca_{0.8}Eu_{0.1}Na_{0.1}MoO_6$  precursor sintered at 873 K were also investigated, and we also found the similar weight loss and thermal behavior for the formation of the  $Sr_2Ca_{0.8}Eu_{0.1}Na_{0.1}MoO_6$  phase above 873 K. Therefore, we conclude that crystalline  $Sr_2Ca_{0.8}Eu_{0.1}Na_{0.1}MoO_6$  phase can start to be partly formed after the decomposition of metal nitrates after 944 K, and then will be formed above 1073 K.



**Fig. 1** TG-DTA curves of  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  dried gel (a) and sintered precursors at 873 K (b)

**XRD analysis**

Two cation sites (Sr at the A-site and Ca at the B-site) in double-perovskite  $\text{Sr}_2\text{CaMoO}_6$  phase can be substituted by  $\text{Eu}^{3+}$ , and previous research also indicates that B-site substitution sample helps in the formation of pure double-perovskite  $\text{Sr}_2\text{CaMoO}_6$  phase [15]. Further, it is found that the introduction of the charge compensators can obviously improve the emission intensity of  $\text{Eu}^{3+}$ -doped  $\text{Sr}_2\text{CaMoO}_6$ . Therefore, B-site-substituted  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  sample was selected in this study, in which  $\text{Na}^+$  acts as the charge compensator. Figure 2 exhibits the XRD patterns of the precursor and the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperatures. As shown in Fig. 2, the XRD pattern of the precursor sintered at 873 K shows complex crystallization phases, including the  $\text{SrMoO}_4$ ,  $\text{CaMoO}_4$ , and  $\text{Sr}_2\text{CaMoO}_6$  phases. When the sintering temperature reaches 1073 K, most diffraction peaks in XRD pattern can be indexed to  $\text{Sr}_2\text{CaMoO}_6$  phase except for the impurity peaks at  $27.7^\circ$ , which is corresponding to the  $\text{SrMoO}_4$  phase [15]. With increasing sintering temperature, the intensity of the



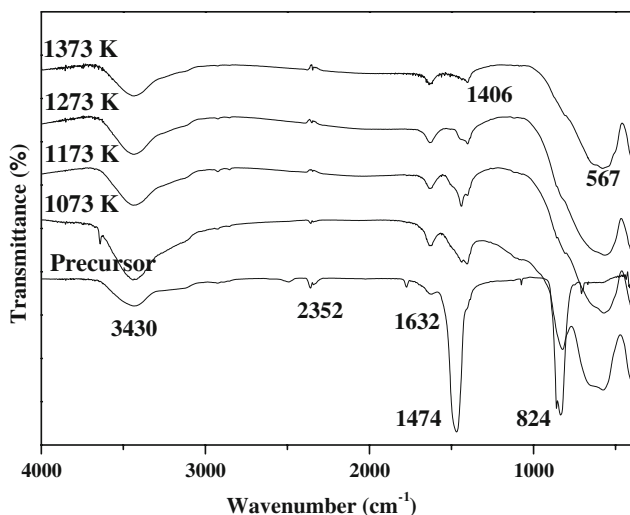
**Fig. 2** XRD patterns of the precursor and the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperatures

impurity peak at  $27.7^\circ$  gradually decreases, and the impurity peak completely disappears when the sintering temperature reaches 1173 K, which is consistent with the TG-DTA analysis. Simultaneously, the peak positions agree well with those of the standard pattern (JCPDS NO. 81-1432) for double-perovskite structure  $\text{Sr}_2\text{CaMoO}_6$ , which belongs to the monoclinic crystal system with a space group of  $P2_1/n$ . Further, according to some previous reports [19, 20], the lattice constants of double-perovskite  $\text{Sr}_2\text{CaMoO}_6$  are:  $a = 5.762 \text{ \AA}$ ,  $b = 5.848 \text{ \AA}$ ,  $c = 8.187 \text{ \AA}$ , and  $\beta = 90.194^\circ$ .

The above results also show that the crystallization temperature of pure double-perovskite  $\text{Sr}_2\text{CaMoO}_6$  phase through the present citric acid-assisted sol-gel method is lower than that in the conventional solid-state reaction ( $1473 \text{ K}$  for 24 h), which demonstrates the most essential advantage of the sol-gel method [15–17].

**FT-IR analysis**

The FT-IR spectra of the as-synthesized precursor sintered at 873 K, and the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperature are shown in Fig. 3. As shown in Fig. 3, the bands at  $3430$  and  $1632 \text{ cm}^{-1}$  are assigned to O–H stretching vibration and H–O–H bending vibration of absorbed water molecular from air, respectively, and it is completely different from coordinated water in compounds [21]. For the FT-IR spectrum of the as-synthesized precursor, the  $1474 \text{ cm}^{-1}$  band is attributed to N–O vibration modes from the starting reactants  $\text{NO}_3^-$ , while no obvious absorption band can be found in this region for the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different



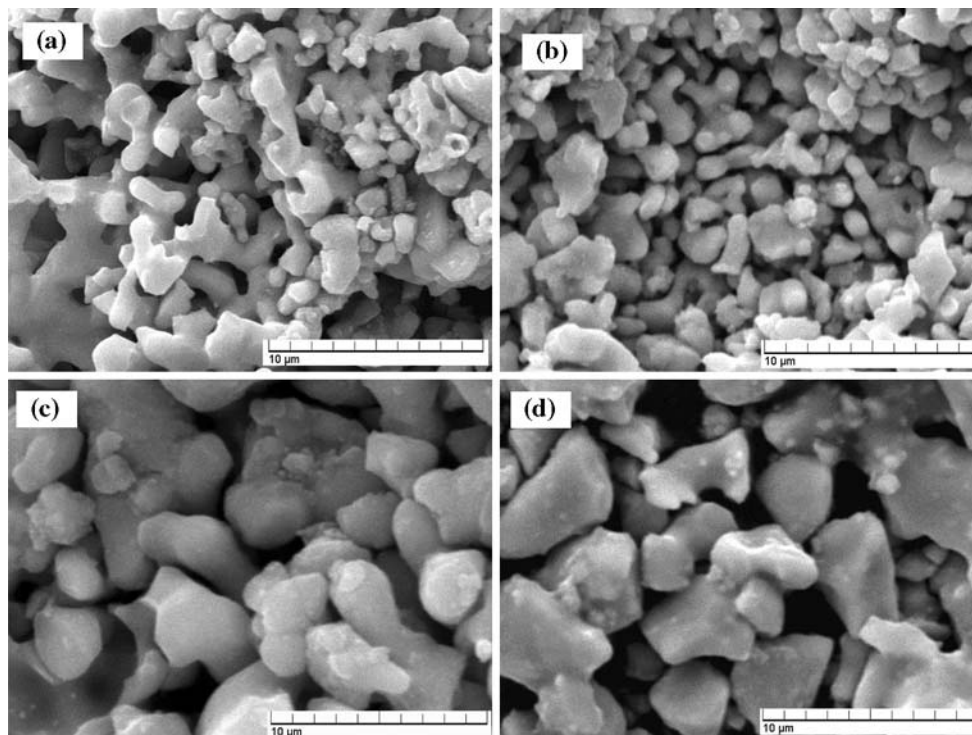
**Fig. 3** FT-IR spectra of the precursor and the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperatures

temperatures. This is also consistent with the previous TG-DTA analysis. The absorption band around  $824\text{ cm}^{-1}$  is related to O–Mo–O stretches of the  $\text{MoO}_4^{2-}$  groups, because of the existence of the  $\text{SrMoO}_4$  impurity phase [15, 22]. And this absorption band disappears for the sample obtained above 1173 K. Furthermore, a strong absorption band around  $567\text{ cm}^{-1}$  is formed when the sintering temperature is above 1073 K, and the four samples have nearly

the same vibration bands in this wavenumber region, which is related to  $\text{MoO}_6^{6-}$  groups in  $\text{Sr}_2\text{CaMoO}_6$  structure [17, 22, 23]. The above results indicate that the products obtained at 1073 and 1373 K are of the same phase  $\text{Sr}_2\text{CaMoO}_6$  with different crystallization.

#### SEM micrographs analysis

In order to further understand the growth process of the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples, we investigated the effects of temperature on the morphology of the products. Figure 4 shows the SEM images of the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples, which is obtained by sintering the precursor at different temperatures (1073, 1173, 1273, and 1373 K) for 8 h. It can be seen from Fig. 4 that there is an obvious grain growth trend with increasing temperature. Figure 4a, as an example, these are the smallest grain size (1–2  $\mu\text{m}$ ). Further, the phosphor powder grains sintered at 1173 K grow up to 2–3  $\mu\text{m}$ , and the phosphor powder has the moderate grain size (3–5  $\mu\text{m}$ ), uniform shaped microstructure at 1273 K. Then the larger grain ( $\sim 5\text{ }\mu\text{m}$ ) can be found when the reaction temperature reaches 1373 K. Compared to the solid-state method, the small particle size and uniform surface morphology of the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples by sol–gel method can better meet the application of phosphors in LED.

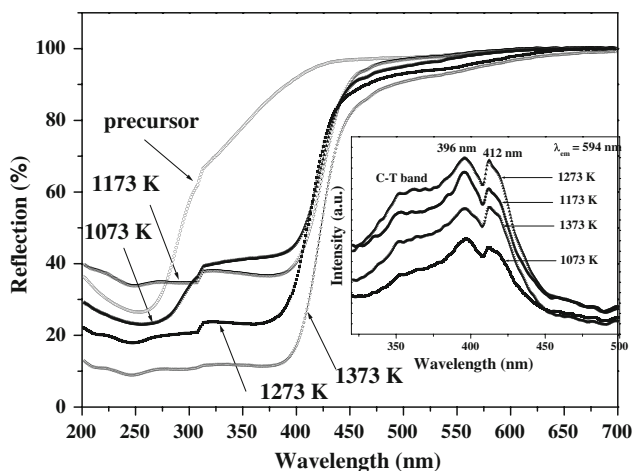


**Fig. 4** SEM images of the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperatures, **a** 1073 K, **b** 1173 K, **c** 1273 K, and **d** 1373 K

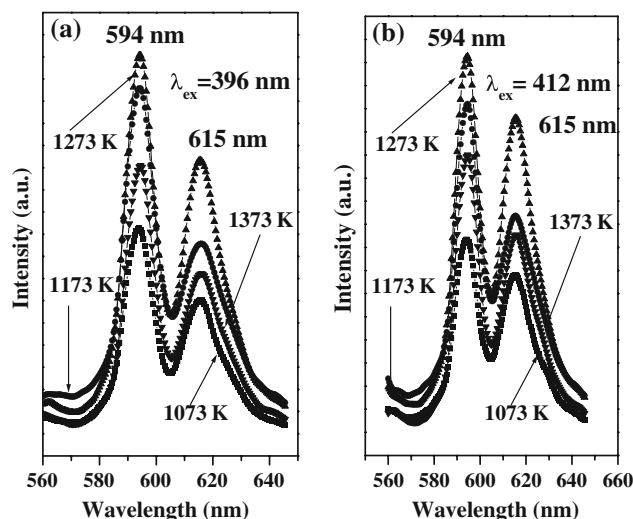


Photoluminescence analysis

In order to investigate the energy absorption of the different samples, Fig. 5 gives the diffuse reflection spectra of the precursor and the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperature. As shown in Fig. 5, broad absorption band is observed for all compositions, and this band is due to charge transfer (CT) transition from oxygen to molybdenum (O–Mo) [24]. However, the largest absorption band for the precursor is centered at 255 nm, which should be ascribed to the  $\text{MoO}_4^{2-}$  groups in the  $\text{SrMoO}_4$  phase [15]. However, when the precursor is secondly sintered above 1073 K, it is observed that the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  shows a platform of high reflection in the wavelength range of 450–700 nm and then starts to decrease obviously from 450 to 200 nm, which is due to the host absorption coming from the  $\text{MoO}_6^{6-}$  groups in  $\text{Sr}_2\text{CaMoO}_6$  structure [15, 16]. However, we cannot find the possible absorption region for  $\text{Eu}^{3+}$  ion on the diffuse reflection spectra, which should be owing to the weak absorption intensities of  $\text{Eu}^{3+}$ . Further, by monitoring the  $^5\text{D}_0\text{--}^7\text{F}_1$  magnetic dipole (MD) transition of  $\text{Eu}^{3+}$  at 594 nm, the inset of Fig. 5 gives the excitation spectra of the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperatures. For every sample, the spectra contain broad absorption band from 320 to 450 nm with peak maximum at 350 nm, and this is due to oxygen to molybdenum CT transition. In addition, there are two obvious characteristic  $\text{Eu}^{3+}$  excitation lines in the excitation spectra, which correspond to the transitions of  $^7\text{F}_0\text{--}^5\text{L}_6$  at 396 nm and  $^7\text{F}_0\text{--}^5\text{D}_2$  at 412 nm, respectively. Further, with increasing temperature, the excitation intensity increases from 1073 to 1273 K, then it decreases at 1373 K, which indicates that the



**Fig. 5** Diffuse reflection spectra and excitation ( $\lambda_{em} = 594$  nm) spectra (*Inset*) of the precursor and the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperatures

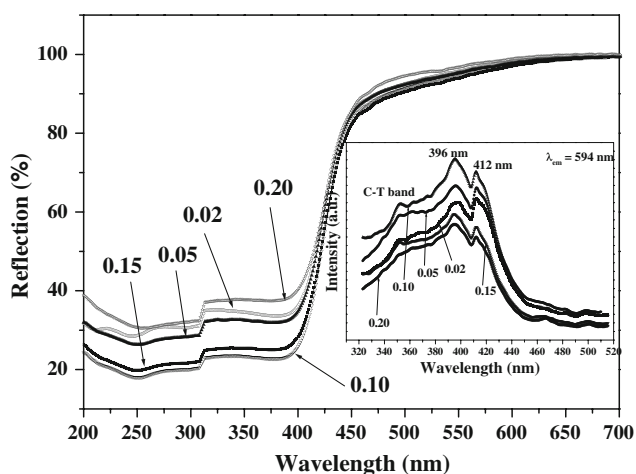


**Fig. 6** Emission spectra of the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples obtained by sintering the precursor at different temperatures, **a**  $\lambda_{ex} = 396$  nm, **b**  $\lambda_{ex} = 412$  nm

sample obtained at 1273 K has the strongest excitation intensity.

Figure 6 gives the sintering temperature-dependent emission spectra of the  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  samples. Upon different excitation wavelengths (396 and 412 nm), we can find that both emission intensities with different sintering temperatures have the same variation trend, and the sample obtained at 1273 K has the strongest emission intensity, which is consistent with the excitation spectra. For the two series samples excited by 396 or 412 nm, two typical emission peaks of  $\text{Eu}^{3+}$  are located mainly in the red region of the spectrum (594 and 615 nm) and are attributable to the  $^5\text{D}_0\text{--}^7\text{F}_1$  and  $^5\text{D}_0\text{--}^7\text{F}_2$  transitions, respectively. We can also find that the relative intensity of  $^5\text{D}_0\text{--}^7\text{F}_1$  MD transition at 594 nm is higher than that of  $^5\text{D}_0\text{--}^7\text{F}_2$  electric dipole (ED) transition at 615 nm. As mentioned earlier,  $\text{Sr}_2\text{CaMoO}_6$  with pseudo-cubic structure has no distortional A- and B-sites in the double-perovskite structure, and the  $\text{Eu}^{3+}$  ions enter the B-sites in  $\text{ABO}_3$  frameworks, which is the center of the cubic cell [15]. The observed characteristics  $\text{Eu}^{3+}$  luminescence in  $\text{Sr}_2\text{CaMoO}_6$  host clearly indicates that the  $\text{Eu}^{3+}$  occupies centrosymmetric site in the currently studied phases.

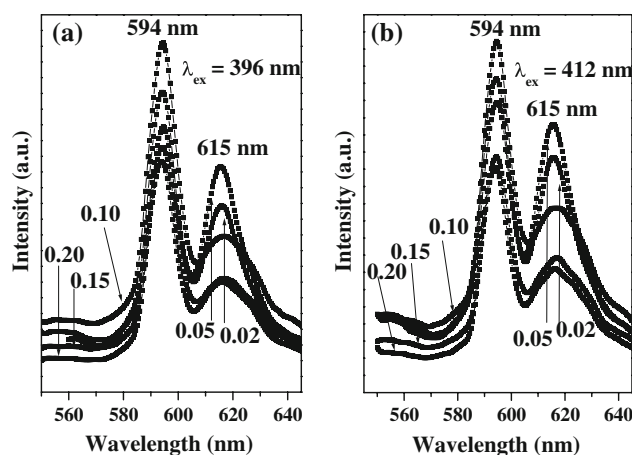
It is generally accepted that effect of  $\text{Eu}^{3+}$  concentration plays an important role in the luminescence properties of the red-emitting phosphor, and the variations of luminescence properties of  $\text{Eu}^{3+}$  concentration-dependent  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  have been investigated in this study. Figure 7 gives the diffuse reflection spectra of  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  phosphors with different  $\text{Eu}^{3+}$ -doping concentrations, which are recorded under the same experimental conditions. All the samples show broad absorption



**Fig. 7** Diffuse reflection spectra and excitation ( $\lambda_{em} = 594$  nm) spectra (*Inset*) of  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  ( $x = 0.02, 0.05, 0.10, 0.15, 0.2$ ) prepared at 1273 K for 8 h

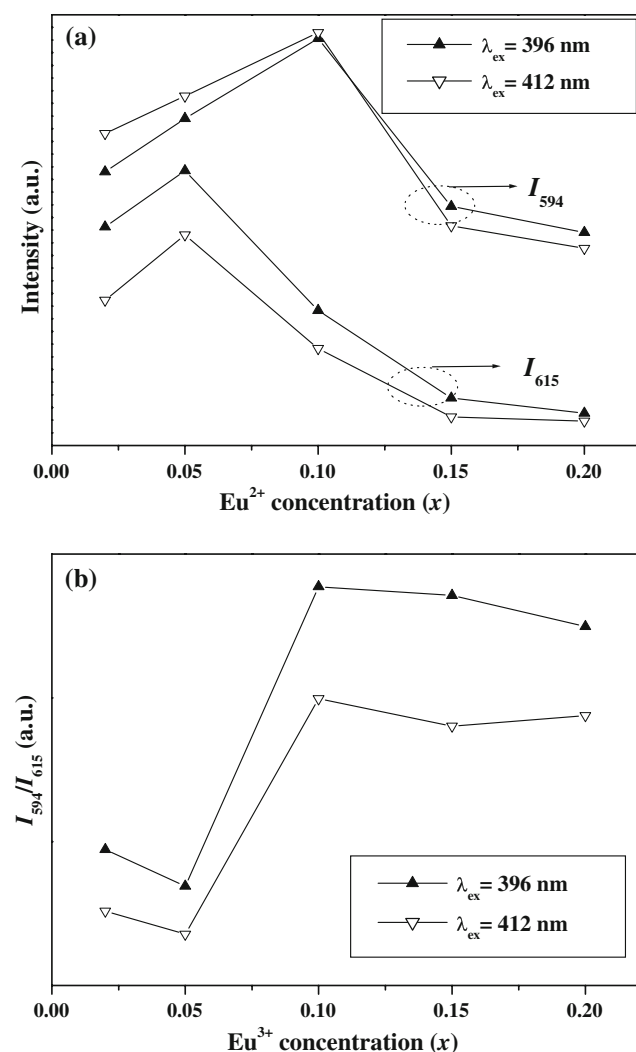
band ranging from 200 to 450 nm, and there are three obvious absorption bands peaking at 251, 307, and 388 nm, respectively. The observed broad absorption bands are assigned to CT transition of the  $\text{MoO}_6^{6-}$  groups in  $\text{Sr}_2\text{CaMoO}_6$  structure. Accordingly, excitation spectra obtained by monitoring the  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$  transition of  $\text{Eu}^{3+}$  at 594 nm for  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  with varied  $\text{Eu}^{3+}$  dopant concentration are presented in the inset of Fig. 7. As stated above, the excitation spectra for various  $\text{Eu}^{3+}$  concentrations are all composed of three characteristic absorption regions, and the first one is the broad absorption band from 320 to 450 nm with peak maximum at 350 nm, which is originated from oxygen to molybdenum CT transition. Two obvious characteristic  $\text{Eu}^{3+}$  excitation lines at 396 and 412 nm are ascribed to the transitions of  ${}^7\text{F}_0\text{--}{}^5\text{L}_6$  and  ${}^7\text{F}_0\text{--}{}^5\text{D}_2$ , respectively. Further, we can also find that  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  sample has the strongest absorption in the excitation spectra.

We should also find that the red emission is observed for all compositions with excitation either in the CT band or in the  $\text{Eu}^{3+}$  levels. The emission spectra obtained by excitation at 396 and 412 nm for  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  ( $x = 0.02, 0.05, 0.10, 0.15, 0.2$ ) are given in Fig. 8a and b, respectively. As seen in Fig. 8, under different  $\text{Eu}^{3+}$  excitations (396 and 412 nm), there are the same emission spectra profiles and variations. A dominant red emission line at around 594 nm, which is due to the  $\text{Eu}^{3+}$  magnetic dipole transition of  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ , is observed in the two excitation wavelengths. However, for the  $\text{Eu}^{3+}$  concentration-dependent emission spectra of  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  phosphors, the relative intensities between  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$  and  ${}^5\text{D}_0\text{--}{}^7\text{F}_2$  transitions have obvious difference. In order to display this variation trend obviously, Fig. 9a gives the



**Fig. 8** Emission spectra of  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  ( $x = 0.02, 0.05, 0.10, 0.15, 0.2$ ) prepared at 1273 K for 8 h, **a**  $\lambda_{ex} = 396$  nm, **b**  $\lambda_{ex} = 412$  nm

emission intensities at 594 and 615 nm as a function of  $\text{Eu}^{3+}$ -doping concentrations for  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  phosphors. As seen in Fig. 9a, for the emission intensities at 594 nm, it is found that the emission intensities under 396 nm have the same variation as that under 412 nm when  $\text{Eu}^{3+}$  concentrations  $x$  increases, the maximum emission intensity was observed for the  $\text{Eu}^{3+}$  concentrations  $x = 0.10$ . As a comparison, although the emission intensities under 396 nm are the same as that under 412 nm when  $\text{Eu}^{3+}$  concentrations  $x$  increases, the maximum emission intensity at 615 nm was observed for the second composition, viz,  $\text{Eu}^{3+}$  concentrations  $x = 0.05$ . Further, Fig. 9b shows the  $\text{Eu}^{3+}$ -doping concentration dependence of the relative emission intensities of  $I_{594/615}$  with  $\text{Eu}^{3+}$  concentration for  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  phosphors. We can find that the relative emission intensities of  $I_{594/615}$  have the same variation. As far as the  $\text{Eu}^{3+}$ -doping concentration is concerned, there is the minimum difference between the emission intensity at 594 nm and that at 615 nm for the  $\text{Eu}^{3+}$  concentrations  $x = 0.05$ . With increasing  $\text{Eu}^{3+}$  concentrations, the variation of the relative emission intensities of  $I_{594/615}$  keeps nearly invariable. As is well known,  $\text{Eu}^{3+}$  is a good probe for the chemical environment of the rare-earth ion because the  ${}^5\text{D}_0\text{--}{}^7\text{F}_2$  transition is very sensitive to relatively small changes in the surroundings, but the  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$  transition is insensitive to the environment [25]. Although no obvious impurity phase can be found in  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  solid solution even when  $x = 0.20$ , this is also testified by our XRD analysis. However, when excess  $\text{Eu}^{3+}$  ions enter the  $\text{Ca}^{2+}$  sites, which is ascribed to the inversion center sites, it will change the environment of  $\text{Eu}^{3+}$  in the  $\text{Sr}_2\text{CaMoO}_6$  host lattice, and ED transition at 615 nm will decrease, then CD transition at 594 nm will be relatively strong.



**Fig. 9** Variation of emission intensities at 594 and 615 nm (a) and the relative emission intensities of  $I_{594/615}$  (b) with  $\text{Eu}^{3+}$  concentration for  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  ( $x = 0.02, 0.05, 0.10, 0.15, 0.2$ ) prepared at 1273 K for 8 h

## Conclusions

A series of double-perovskite  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  red-emitting phosphors was prepared by the citric acid-assisted sol-gel method.  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  phosphor was selected to study the thermal behavior, phase structure, microstructure, and photoluminescence property under different sintering temperatures. The optimum synthesis temperature by sol-gel process can be decided as 1273 K. And at this temperature,  $\text{Sr}_2\text{Ca}_{0.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{MoO}_6$  phosphor with pure phase, uniform microstructure, and optimum luminescence properties can be found. The photoluminescence studies on  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  ( $x = 0.02, 0.05, 0.10, 0.15, 0.2$ ) show that a dominant red emission line at around 594 nm is observed under different  $\text{Eu}^{3+}$

excitations (396 and 412 nm).  $\text{Eu}^{3+}$ -doping concentration-dependent emission spectra investigations of  $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$  phosphors indicate that there are the minimum differences between the emission intensity of  ${}^5\text{D}_0\text{-}{}^7\text{F}_1$  transition at 594 nm and that of  ${}^5\text{D}_0\text{-}{}^7\text{F}_2$  transition at 615 nm when the  $\text{Eu}^{3+}$  concentrations  $x = 0.05$ . Since  $\text{Eu}^{3+}$  ions enter the inversion center  $\text{Ca}^{2+}$  sites, the intensity of  ${}^5\text{D}_0\text{-}{}^7\text{F}_1$  transition at 615 nm will decrease, then the emission of  ${}^5\text{D}_0\text{-}{}^7\text{F}_2$  transition at 594 nm will be relatively strong. Therefore, the variation of the above two emission intensities keeps nearly invariable with increasing  $\text{Eu}^{3+}$  concentration.

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## References

- Nakamura S, Fasol G (1997) The blue laser diode: GaN based light emitters and lasers. Springer, Berlin, p 19
- Nakamura S, Snoh M, Mukai T (1993) Appl Phys Lett 62:2390
- Chan T, Liu R, Baginskiy I (2008) Chem Mater 20:1215
- Park JK, Kim CH, Park SH, Park HD (2004) Appl Phys Lett 84:1647
- Neeraj S, Kijima N, Cheetham AK (2004) Chem Phys Lett 387:2
- Liu J, Lian H, Shi C (2007) Opt Mater 29:1591
- Uheda K, Hirotsuki N, Yamamoto Y, Natio A, Nakajima T, Yamamoto H (2006) Electrochem Solid-State Lett 9:H22
- Sivakumar V, Varadaraju UV (2005) J Electrochem Soc 152: H168
- Wang J, Jing X, Yan C, Lin J, Liao F (2005) J Electrochem Soc 152:G534
- Zhang Q, Wang J, Yu R, Zhang M, Su Q (2008) Electrochem Solid-state Lett 11:H335
- Wang J, Jing X, Yan C, Lin J, Liao F (2006) J Lumin 121:57
- Guo C, Chen T, Luan L, Zhang W, Huang D (2008) J Phys Chem Solids 69:1905
- Shi S, Gao J, Zhou J (2008) J Electrochem Soc 155:H525
- Chiu C, Liu C, Huang S, Chen T (2008) J Electrochem Soc 155:J71
- Ye S, Wang C, Jing X (2008) J Electrochem Soc 155:J148
- Ye S, Wang C, Liu Z, Lu J, Jing X (2008) Appl Phys B 91:551
- Sivakumar V, Varadaraju UV (2008) J Solid State Chem 181: 3344
- Guo C, Zhang W, Luan L, Chen T, Cheng H, Huang D (2008) Sensor Actuat B-Chem 133:33
- Prior T, Couper V, Battle P (2005) J Solid State Chem 178:153
- Teraoka Y, Wei MD, Kagawa S (1998) J Mater Chem 8:2323
- Tomaszewicz E (2006) Solid State Sci 8:508
- Lei F, Yan B (2008) J Solid State Chem 181:855
- Anderson MT, Greenwood KB, Taylor GA, Poeppelmeier KR (1993) Prog Solid State Chem 22:197
- Lei F, Yan B, Chen H (2008) J Solid State Chem 181:2845
- Pang ML, Liu XM (2005) J Mater Res 20:2676