Short Communication

Synthesis of mesoporous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ energy storage carriers using cetyl trimethyl ammonium bromide as a template

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Abstract

In this study mesoporous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ energy storage carriers were successfully prepared using cetyl trimethylammonium bromide (CTAB) as a template. Mesoporous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ can be obtained at a relatively low temperature of 950 °C with the addition of CTAB. The sample shows good porosity and energy storage performance. The pore diameter of the sample is distributed uniformly from 2 to 11 nm. The optical storage capability of the samples was investigated by studying the photoluminescence decay curves, which revealed that the afterglow time of the product could be improved by optimizing the amount of CTAB. Porous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ can therefore serve as a promising energy-storage carrier.

Keywords: Ceramics, Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$, porous materials, energy storage, luminescence

I. Introduction

Afterglow refers to the light emission of the phosphors that persists for a certain duration after excitation owing to their characteristic of long-lasting phosphorescence and glowing at night, and can be applied in photoluminescence, lighting, emergency warning signboards, crafts, biological markers, watch dials, luminous paints, traffic signs, etc. 1-3. However, most of these materials have some serious shortcomings such as poor water resistance and single color restrictions 4,5, limiting their application. In order to overcome these drawbacks, a new luminescent material named silicate long-afterglow phosphor has been studied by some researchers because rare earth-doped silicates exhibit many excellent properties such as good chemical stability, water resistance, ultraviolet-irradiation stability, high brightness and a long afterglow time 6-9. So long-afterglow silicate phosphors have seen rapid development over the past few decades 10-12. Sr$_2$MgSi$_2$O$_7$ is one of these silicate materials, and owing to its excellent characteristics and easy processing, considerable efforts have been focused on the growth and optical properties of rare-earth-doped Sr$_2$MgSi$_2$O$_7$-based phosphors.

The studies on Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ are currently focused on synthesis techniques, such as the solid-state reaction method 13,14 and the sol-gel method 15. The sintering temperatures are 1200 °C and 1050 °C respectively and the released energy of Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ cannot be used efficiently in darkness, which is effectively a waste of energy.

While porous material is widely applied in composite material owing to its large specific surface area and high porosity, porous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ can improve the utilization of solar energy. Qingzhou Zhai 16 prepared a mesoporous SBA-15 molecular sieve to evaluate its application as a nimodipine drug delivery system. Results demonstrated that nimodipine can be selectively doped inside the pores of the mesoporous SBA-15 molecular sieve and the medical effect of nimodipine was improved. Porous material is fit to act as a carrier in composite material. We fabricated a porous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ energy storage carrier prototype at 950 °C, which represents a breakthrough in the synthesis of Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$. In addition, the sample showed excellent energy-storage performance, good luminescence and a long afterglow time, which demonstrated that porous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ is a promising candidate for future commercial energy-storage carriers.

Compared with our previous research 17, the temperature of sample preparation was reduced by 100 °C from 1050 °C to 950 °C. The sample exhibits a high degree of crystallinity, less impurity phase, in addition the pore size distribution of the sample is uniform from 2 to 11 nm, compared to samples from previous work, which were prepared in the larger pore size distribution within the range of 10–50 nm, with an unconcentrated distribution. The emission intensity of the sample and the afterglow effect has been enhanced.

II. Experimental

Sr(NO$_3$)$_2$, Mg(NO$_3$)$_2$, Eu$_2$O$_3$, and Dy$_2$O$_3$ were first individually dissolved in HNO$_3$ (30 wt%) and the resulting mixtures were denoted A, B, C, and D, respectively. The Eu$^{2+}$/Dy$^{3+}$ molar ratio was selected as 1/2. Next, H$_3$BO$_3$ was dissolved in distilled water and used as fluxing medium to reduce the melting temperature during the preparation of the sample.
sintering process and denoted solution ‘E’. Furthermore, a certain amount of TEOS was dissolved in ethanol. Afterwards, the solutions A, B, C, D and E were mixed together until the dissolution was complete, and then the mixed solution was dissolved in the TEOS/ethanol solution. CTAB was then added to the mixed solution. The pH value was adjusted to 7–10 by dropping NH₃·H₂O into the mixed solution. Under continuous magnetic stirring, the resulting solution was subsequently heated in a water bath at 70 °C for a certain period of time to produce the Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ sol and then dried at 70 °C for 1–2 days to produce a dry gel, followed by sintering at 900 to 1100 °C in a weakly reducing atmosphere.

X-ray diffraction (XRD) patterns were recorded using an x-ray diffractometer (Rigaku D/Ma-2500) operating with Cu Kα radiation (λ = 0.15406 nm). The samples were further investigated by means of scanning electron microscopy (SEM, Hitachi Limited, Japan), transmission electron microscopy (TEM, Jeol Limited, Japan) and nitrogen physisorption analysis (Quantachrome Instruments, America). The luminescence spectra were recorded with a fluorescence spectrometer (Hitachi F-7000) equipped with a 150 W Xe lamp at a spectral resolution of 0.1 nm. Long-time decay curves were recorded under the same conditions with an accuracy of ±3 μs.

III. Results and Discussions

Fig. 1 shows the XRD patterns recorded for the porous Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ carriers with the CTAB/TEOS mass ratio 0/1, 0.08/1, 0.16/1, 0.24/1, and 0.32/1, and sintering at 950 °C. As shown in Fig. 1, all the ratios can obtain Sr₂MgSi₂O₇ as the main crystalline phase except the sample without CTAB. When the mass ratio is 0.16/1, the main phase of the peak intensity is strongest. However, the intensity of the diffraction peak associated with the Sr₂MgSi₂O₇ phase decreased and SrMgSi₂O₄, MgSiO₃ phase appeared when the CTAB/TEOS mass ratio was eventually increased to 0.32/1, which may be attributed to the extra CTAB reacting with substances in solution. The addition of CTAB promotes the formation of the sample, which may be because CTAB as a surfactant improves the activity of each substance.

Fig. 2 shows the XRD patterns recorded for the mesoporous Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ carriers after sintering at 900 °C, 950 °C, 1000 °C, 1050 °C and 1100 °C with the CTAB/TEOS mass ratio at 0.16:1, respectively. At all the temperatures, the main crystalline phase is Sr₂MgSi₂O₇ and the peaks are indexed to be tetragonal Sr₂MgSi₂O₇ structure (JCPDS card: 75–1736). With the increase in the temperature from 900 °C to 1050 °C, the intensity of the diffraction peak associated with the Sr₂MgSi₂O₇ phase increased. When the sintering temperature was increased to 1050 °C, the main crystalline phase was Sr₂MgSi₂O₇, and the Sr₂MgSi₂O₇ showed a high degree of crystallinity. Until the temperature increased to 1100 °C, the intensity of the diffraction peak decreased.

Representative SEM micrographs of the mesoporous surfaces of the Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ carrier samples after calcination at 900, 950, 1000, 1050 and 1100 °C, respectively are shown in Fig. 3. The channels are formed by particle accumulation. There are a lot of channels when the samples are sintered at 900 °C, but crystals do not grow fully. When the sintering temperature was increased to 950 °C, the crystals grew significantly and the porosity became higher and was distributed more uniformly. When the sintering temperature was increased to 1000 °C, conductivity became higher and was distributed more uniformly. When the sintering temperature was increased to 1050 °C, a few channels appeared. When the temperature was increased further to 1100 °C, crystallization occurred and no channels are visible. The structure of the pores was well-preserved when the samples were sintered at 900 and 950 °C, while with the increase in the sintering temperature, the pores collapsed until they disappeared at 1100 °C.

Fig. 4 compares the excitation (a) and emission (b) spectra of the mesoporous Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ carrier samples with different CTAB/TEOS ratios after sintering at 950 °C. The excitation spectra were monitored at λem = 467 nm. All spectra feature a similar broad absorption band at around 277 nm and 355 nm. The excitation band at 355 nm in Fig. 4(a) is a host absorption
band attributed to the following transition: $^{4}f_{65}d_{1} \rightarrow ^{4}f_{7}(8S_{7/2})$. There is no characteristic emission associated with Dy$^{3+}$ and Eu$^{3+}$, which suggests that Dy$^{3+}$ is not the luminescence center and Eu$^{3+}$ has been completely reduced to Eu$^{2+}$. The emission spectra were recorded in the range from 425 to 550 nm after excitation at 355 nm, which is consistent with the data published by Ye et al.\textsuperscript{18}. When the emission spectra of the samples with different CTAB/TEOS mass ratios are compared, the intensity of the emission peak at 467 nm is lowest for a CTAB/TEOS ratio of 0/1. When the CTAB concentration was increased, the intensity of the emission increased. When the CTAB/TEOS is 0.16/1, the peak intensity was strongest. However, with the increase in the content of CTAB, the peak intensity gradually weakened. Extra CTAB reacts with the substance in the solution, effecting the form of Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$, thus affecting the luminescence property of the sample, which is consistent with the XRD results.

Fig. 3: SEM images of the mesoporous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ carrier material after sintering at different temperatures with the mass ratio of 0.16:1.

Fig. 4: (a) Excitation and (b) emission spectra with different CTAB/TEOS mass ratio after sintering at 950 $^\circ$C.

Fig. 5 shows the excitation (a) and emission (b) spectra of the mesoporous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ carrier samples after sintering at 900 $^\circ$C, 950 $^\circ$C, 1000 $^\circ$C, 1050 $^\circ$C and 1100 $^\circ$C with a CTAB/TEOS ratio of 0.16:1. The excitation spectra were monitored at $\lambda_{\text{em}} = 467 $ nm. All spectra feature a similar broad absorption band at around 277 nm and 355 nm. The excitation band at 355 nm. The calcination temperature has no effect on the excitation and emission peak position of the sample, but the intensity varies. The highest brightness was recorded after sintering at 950 $^\circ$C. The sample sintered at 900 $^\circ$C also showed the luminescent properties, but owing to the low crystallinity the luminescence is low. The glass phase appeared after sintering at 1100 $^\circ$C, so the intensity of the peak is relatively low. When sintered at 1000 $^\circ$C and 1050 $^\circ$C, the sample showed good luminescence properties.

Fig. 5: (a) Excitation and (b) emission spectra and with CTAB/TEOS mass ratio of 0.16:1 after sintering at different temperature.
Fig. 6 shows the decay curves featuring a fast-fading component and a slow-fading component which can be modeled using the following formula: \( I = I_1 e^{-t/a_1} + I_2 e^{-t/a_2} \).

The short survival time of Eu\(^{2+}\) is responsible for the fast-fading component, while the slow-fading component is attributed to the trapping level of the Dy\(^{3+}\) ions. After the sample is sintered at 950 °C for 2 h, the brightness of the sample is high, and both the fast fading and the slow fading time are relatively long. The sample sintered at 900 °C also showed the fastest decay owing to incomplete crystal growth of the low Sr\(_2\)MgSi\(_2\)O\(_7\) concentration. When the sintering temperature was increased to 1000 °C, the concentration of Sr\(_2\)MgSi\(_2\)O\(_7\) in the sample increased. However, the sample sintered at 1050 °C showed a long afterglow time and a relatively high brightness because of the good growth of the Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\), Dy\(^{3+}\) phase. The glass phase appeared after sintering at 1100 °C for 2 h, the intensity of the luminescence property is higher, but the decay rate is fast so the glass phase did not contribute to the sample’s energy-storage carrier performance.

Fig. 7 shows the decay curves of the sample prepared at different pH value. The pH value has a considerable impact on the energy storage properties of the samples. When pH = 7, the sample exhibits excellent energy storage, when the pH value increases, the energy storage performance weakens until at pH = 10, the energy storage performance disappears. Therefore, for preparation of the samples, the optimum pH is 7.

TEM micrographs of the sample sintered at 950 °C for 2 h are shown in Fig. 8. The TEM images in Fig. 8 highlight the sample’s microstructure. Besides, as illustrated by the high-resolution TEM images, a localized ordered channel structure appeared, furthermore the distribution in the sample is clear and uniform, making the Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\), Dy\(^{3+}\) samples a suitable carrier material.

Fig. 9 illustrates the pore size distribution of the porous Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\), Dy\(^{3+}\) energy storage carriers. The pore size distribution was calculated according to the BJH method for nitrogen desorption curves. The curve shows that the pore size ranged from 2 to 11 nm, which is consistent with the TEM results. The pore diameter distribution of the carrier material provided the preconditions for a particular size of the material load.
IV. Conclusions

Mesoporous Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ energy-storage carriers were successfully prepared using cetyl trimethylammonium bromide (CTAB) as a template. Based on XRD and SEM investigations, sintering at 950 °C in a weakly reducing atmosphere was found to yield the best results concerning the microstructure, phase composition and crystallinity of the resulting sample. The SEM and TEM results indicate that a material with a pore structure suitable for application as an energy-storage carrier was obtained after sintering at 950 °C for 2 h, and the pore size distribution was uniform, ranging from 2 to 11 nm. At the same time, the best initial brightness and longest afterglow time were obtained for sintering at 950 °C for 2 h, as revealed by the fluorescence analysis and the luminescence decay curves. The excitation wavelength was determined at 467 nm, which is the same as the excitation wavelength of the fluorescence analysis and the luminescence of the resulting sample. The SEM and TEM results indicate that a material with a pore structure suitable for application as an energy-storage carrier was obtained after sintering at 950 °C for 2 h, and the pore size distribution was uniform, ranging from 2 to 11 nm. At the same time, the best initial brightness and longest afterglow time were obtained for sintering at 950 °C for 2 h, as revealed by the fluorescence analysis and the luminescence decay curves. The excitation wavelength was determined at 467 nm, which is the same as the excitation wavelength and emission spectra.

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