Microwave-promoted pure host phase for red emission CaS:Eu^{2+} phosphor from single $CaSO_4$ precursor and the photoluminescence property*

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We report a novel approach to obtaining a classical blue-green excitable CaS:Eu^{2+} phosphor with desired red emission by microwave (MW) firing procedure in the absence of adding elemental sulphur. The disturbing effect of MW electromagnetic field on decomposition of $CaSO_4$ into CaS activated by europium is distinctly observed to give pure host phase without adding any elemental sulphur and carbon. The host phase evolution is observed to be highly dependent on the variation of applied MW power from X-ray diffraction (XRD) patterns and the corresponding photoluminescence (PL), and a maximum PL intensity at 1100 W of MW power is acquired for the obtained purer host phase. The non-thermal and non-equilibrium effects by MW are revealed to correlate with the interaction between polar structure of the host and applied electromagnetic field. The results demonstrate an optional procedure to prepare this red-emitting phosphor in an effective, environment-friendly and scalable approach for phosphor production in the application of bio-illumination for plant cultivation and artificial photosynthesis.

Keywords: red emission, calcium sulfide, microwave energy

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1. Introduction

Red emission from phosphor or light-emitting diode (LED) is of great importance in the fields of warm-white illumination and display. In warm white LED, the red AlGaInP chip array is used with blue InGaN chip in chip-on-board (COB) packaging procedure to obtain white light with a higher color rendering index while the blue and near ultraviolet (NUV) excitable rare earth (RE) doped nitride-based phosphor with well-recognized high thermal stability is used as red compensate color for warm white. Other red emission phosphors can also be exemplified such as $CaAlSiN_3$:Eu^{2+} [1] and quantum dots (QDs).[2] For the present concern, the materials of rare-earth-doped CaS crystals have been extensively studied,[3–5] especially a very classical CaS:Eu^{2+} phosphor has long been a concern with its outstanding blue–green excitable properties and effective cost, allowing its broad applications in phosphor converted (pc) white LEDs[6] and light conversion of sunshine.[7] Excepting the chemical and thermal stability realized by coating silica,[8,9] alumina,[10,11] or BN layers,[12] controllable synthesis of pure host phase of CaS:Eu^{2+} phosphor[13–17] remains one of challenging problems to be solved. Generally, the excessive additions of elemental sulphur and carbon are used in traditional high-temperature solid state synthesis procedure, which easily leads to high cost and emission threat to the environment.[18–20]

MW energy has long been used in aqueous or solvent solution processing of materials such as in organic synthesis.[21] We previously successfully synthesized a 660-nm-featured $(Ba, Sr)_3MgSi_2O_8$:$0.06Eu^{2+}$, $0.1Mn^{2+}$ (*A*MS-EM, *A* = Ba, Sr, Ca) phosphor with MW procedure.[22] For the present interest in preparing a very classical CaS:Eu^{2+} phosphor, the excessive addition of elemental sulphur to the mixture of raw materials has long been adopted so as to obtain pure host phase.[23–25] Zhang *et al.* synthesized CaS:Mn^{2+}, Eu^{2+} phosphor in microwave field.[25] With an attempt to be free of adding elemental sulphur with MW energy procedure, we here report the synthesis of the phosphor of CaS:Eu^{2+} by using the MW energy to decompose $CaSO_4$ directly as the only precursor, and some MW non-thermal mechanisms involved in the process will be discussed.

2. Experiment

The raw materials used for synthesis include 99.5%$CaSO_4$, 99.99%Eu_2O_3, and 99.5%NH_4Cl. The amount

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of europium in stoichiometric CaS:Eu^{2+} was set to be 0.3 mol% per mole of $CaSO_4$ by adding Eu_2O_3. A small amount of about 2.5-wt% NH_4Cl was used as flux. The starting material was well mixed in an agate mortar with a small amount of alcohol followed by drying at 80 °C for two hours. The dried powders were placed first in a covered corundum crucible then placed in another bigger-sized ZrO_2-doped corundum crucible. The gap between two crucibles was filled with carbon to generate reducing atmosphere of CO. The duration for firing was set to be 90 minutes upon placing the crucibles in an MW furnace (1.5 kW, 2.45 GHz, maximun temperature 1600 °C, HAMiLab-V1500, Synotherm Ltd, China).

The crystallographic data of as-prepared samples were investigated by X-ray power diffraction (XRD) on a diffractometer (Rigaku D/max-2500/p c, Japan) with a graphite monochromator using Cu-K α radiation ($\lambda = 0.154062$ nm). The photoluminescence (PL) and photoluminescence of excitation (PLE) spectra of samples were recorded on a fluorescence spectrometer equipped with a xenon light source (Hitachi F-4600, Japan). All of these measurements were carried out at room temperature.

3. Results and discussion

3.1. MW-induced chemical reaction

Figure 1 shows X-ray diffraction (XRD) patterns of a typical sample prepared by MW procedure at 1000 °C for 10 minutes and other sample by the solid state (SS) method at 1000 °C for 30 minutes without introducing H_2. Upon applying MW 1000-W power to reaction system and firing at 1000 °C for 10 minutes, the obtained sample consists of a mixture of CaS and CaO, while another sample that is prepared by SS upon firing at 1000 °C for 30 minutes in a muffle furnace consists of CaS and un-reacted $CaSO_4$. These results seem to reveal that the MW field leads to distinctive decomposition of $CaSO_4$ into CaS compared with SS firing procedure.

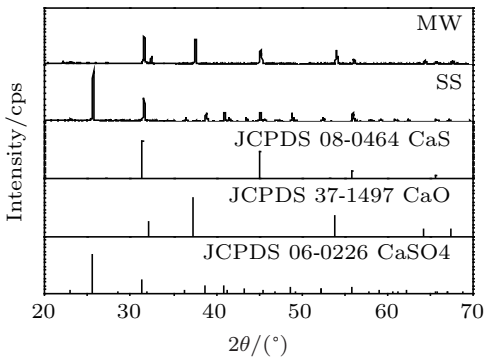


Fig. 1. X-ray diffraction (XRD) patterns of the typical as-prepared samples by microwave (MW) firing and solid state (SS) synthesis in the absence of introducing H_2 respectively.

From XRD results, it is observed that the MW-effected reaction may take place in the absence of adding elemental sulphur and carbon according to reaction Eq. (1)

$$CaSO_4 \xrightarrow[MW]{} CaS(s) + CaO(s) + O_2(g)\uparrow + SO_2(g)\uparrow . \quad (1)$$

In this case, no phase of $CaSO_4$ in the raw material is detected, indicating a possible non-equilibrium reaction mechanism involved in the MW firing procedure to lead to full decomposition of $CaSO_4$. Furthermore, MW parameters need to be optimized so as to more effectively suppress the formation of any impurity.

3.2. Evolution of phase with power supply variation and PL properties

Figure 2 shows the XRD patterns of as-synthesized phosphors as fired for 90 minutes with varied MW power supply. As the MW power increases, the amount of calcium sulfate gradually decreases then disappears finally while that of calcium oxide gradually increases. Beyond 1100 W, the decomposition of $CaSO_4$ is fully completed and the composition of reacted product consists of only CaS and CaO. Table 1 shows the mass fraction of each sample in terms of calculated results by the method of K value through using XRD datum.

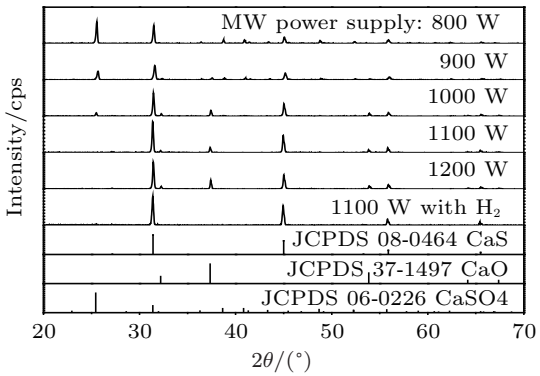


Fig. 2. X-ray diffraction patterns of samples that are prepared at various MW powers for 90 minutes without H_2 introduction, and at a fixed 1100-W MW power for 90 minutes with H_2 introduction.

Table 1. Phase composition of as-received CaS-based samples at different MW powers (mass%).

MW power supply/W	CaS	$CaSO_4$	CaO
800	33.98	66.02	0
900	65.28	28.57	6.15
1000	77.25	8.35	14.40
1100	81.66	0	18.34
1200	71.74	0	28.26

In particular, for the sample coexisting with CaS and CaO, we add a high volume percentage of hydrogen content to the firing furnace system. It is found that the X-ray diffraction pattern of as-received sample at 1100 W with a mixture of H_2 (75%) and N_2 (25%) for 90 minutes firing indicates the formation of nearly pure CaS phase in the absence of any other

impurities. This phenomenon probably indicates that with the aid of MW electromagnetic effect, the hydrogen has effectively deprived the oxygen from CaO to give CaS thermodynamically. This result implies that as long as an appropriate hydrogen atmosphere is introduced into the reaction system, MW-disturbed pure CaS phase is obtainable.

Figure 3 depicts the luminescence spectra of the samples prepared at different MW powers. These phosphors are all excitable in a wavelength range from 250 nm 580 nm. In particular, these phosphors exhibit a 476-nm excitable 654-nm peaked red emission. The intensity distinctly increases with increasing microwave power and reaches a maximum at 1100 W. Corresponding to the XRD patterns of CaS at 1100 W of MW power, the introduction of high-content hydrogen atmosphere distinctly increases the PL intensity.

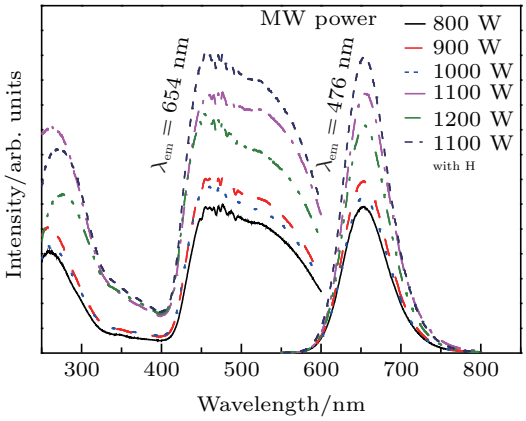


Fig. 3. (color online) PL and PLE emission and excitation spectra of as-prepared samples at various MW powers.

3.3. MW-aided decomposition mechanisms with MW non-thermal effect

In general, electromagnetic field in MW firing will induce some thermodynamic non-equilibrium reactions that generally do not happen in a high-temperature equilibrium system. It has been established that the capability of MW heating is based on the ability for the material to absorb high frequency electromagnetic energy and convert it into heat. This process is due to the dipolar polarization of the molecules or atomic radicals. For CaS atomic structure, figure 4(a) shows that the center of positive charges does not coincide with the center of negative charges and there exist some electric dipole moments like Ca–O and S–O in the crystal structure of calcium sulfate. Hence the atomic structure of $CaSO_4$ can be classified into polar dielectric for its atoms with dipole moment. As $CaSO_4$ is subjected to MW electromagnetic field, the polarization of dipole transformation plays a key role. The important factor that affects MW heating process lies in the dielectric property of $CaSO_4$. Dielectric property of material acts as an effective indicator to predict the viability of heating effect due to the MW energy. For a dielectric material, the property to absorb and store electromagnetic energy was given by the complex permittivity.[26,27] As the material is placed in an MW field with a high frequency of 2.45 GHz, the polarization of dipole transformation does not follow the frequency of the electric field, leading to the diminishing total polarization. This decrease in effective polarization characterizes the decrease in original dielectric constant and the increase in loss factor of the material. As a result, the realignment occurs a million times per second, which results in internal friction of molecules, causing the material to have a volumetric heating and thus rapidly. Meanwhile, owing to the difference in electric dipole moment between Ca–O and S–O, their polarization rates are not the same as in the high frequency magnetic field. As the result of different relaxation times, the imbalance of the entire system is enhanced, which promotes the decomposition of $CaSO_4$ and the replacement of O from Ca–O by S atom to form CaS.

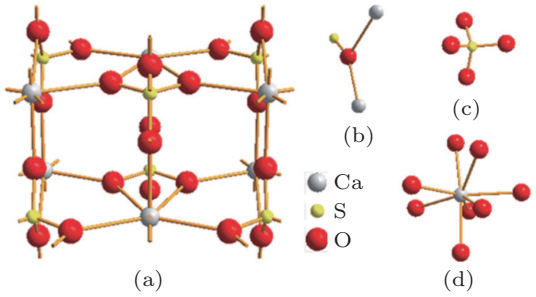


Fig. 4. (color online) (a) Crystal structure of calcium sulfate; (b) Coordination environment of O; (c) Coordination environment of S; (d) Coordination environment of Ca.

The mechanisms involved in this process may be that the non-thermal effect of microwave energy plays a key role to give purer host phase. Figure 4(b)–4(d) show the coordination environments of O, S, and Ca atoms respectively in the crystal structure of calcium sulfate. We find that each Ca atom is surrounded by two 12 O atoms and each S atom is surrounded by 4 O atoms which are in a relatively symmetrical crystal field environment, but each O atom is surrounded by two Ca atoms and one S atom. In addition, the four atoms are in the same plane. Hence the crystal field environment of O atom is very asymmetrical. When these atoms are in the same high frequency electromagnetic field, the crystal field of O atoms is first greatly affected and the original balance between O atoms is weakened. Thus O atoms may first get rid of the shackles of the crystal structure and the combining probability between Ca and S atoms is increased, leading to the formation of pure CaS preferable to other impurity species.

As to the chemical stability of CaS host phosphor, we carry out accelerating ageing measurement at 60 °C and 80% relative humidity. The photoluminescence (PL) spectra of

$CaS:Eu^{2+}$ particles with and without being coated by alumina are evaluated in the reference of Avci *et al.*'s work.[28]

Figure 5 shows the PL emission spectra of uncoated $CaS:Eu^{2+}$ and coated $CaS:Eu^{2+}$ by alumina samples after the accelerating ageing conditions of 60 °C and 80% relative humidity for different durations at an excitation wavelength of 476 nm. Figure 5(a) is related to the PL intensity degradation of uncoated phosphor, and figure 5(b) indicates the reduction of coated sample with alumina layers. It can be shown that during the first 12 hours the emission intensity of uncoated sample decreases faster than that of the coated sample. After 24 hours, the emission intensity of the coated phosphor reaches about 83% of its initial value, while the emission intensity of uncoated sample decreases only to around 61%. The results reveal that the alumina layer is effective to prevent the $CaS:Eu^{2+}$ particles from decomposition in the accelerating ageing process. Hence the property of $CaS:Eu^{2+}$ phosphor against moisture is strongly enhanced.

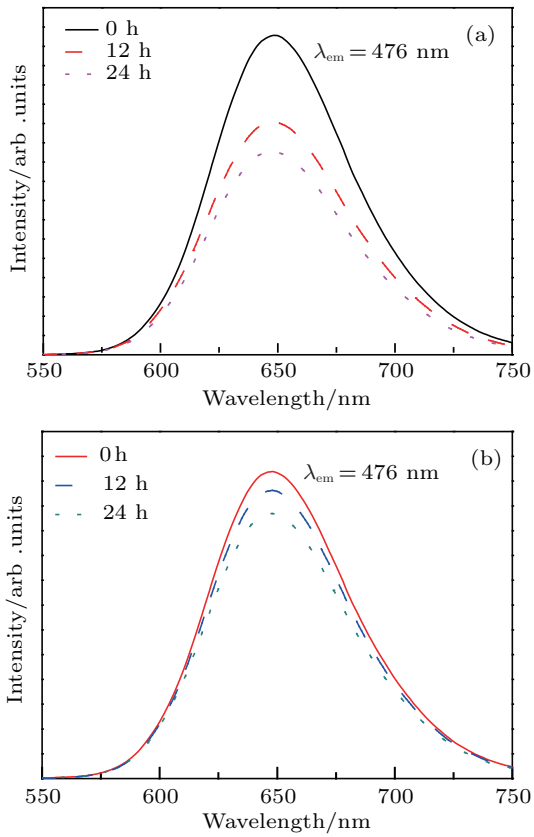


Fig. 5. (color online) (a) PL emission spectra of uncoated $CaS:Eu^{2+}$ samples treated in a 60-°C and 80%-relative humidity environment for different times; (b) PL emission spectra of coated $CaS:Eu^{2+}$ samples treated in 60-°C and 80%-relative humidity environment for different times.

4. Conclusions

Upon introducing MW energy into the $CaSO_4$ decomposition system, the suppression of impurities coexisting with CaS host phase can be realized even without adding elemental sulphur or carbon in such a non-equilibrium thermodynamic way. Through optimization by introducing high volume percentage of hydrogen, pure host phase for $CaS:Eu^{2+}$ can be obtained due to MW electromagnetic effect. An optimized combination of process parameters with MW firing procedure provides a fast, cost-effective route to obtain those non-oxide-based phosphor systems such as the present calcium sulfide doped with Eu^{2+} serving as a red light-emitting phosphor.

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