Preparation Conditions of CaS:Ce Phosphors from CaSO₃:Ce·1/2H₂O

Hiroshi MATSUI, Hironobu OKAMOTO*, Kohei INO*, Genzo HASHIZUME and Gin-ya ADACHI**
(Industrial Research Institute of Hyogo Prefecture, Yukihira-cho, Suma-ku, Kobe, 654
*San-esu Gypsum Co., Ltd., **Department of Applied Chemistry,
Faculty of Engineering, Osaka University)

We have shown the preparation conditions of a green emitting CaS:Ce phosphors from CaSO₃:Ce·1/2H₂O. The precipitation reaction between a CaCl₂ solution and a Na₂SO₃ solution gave the sphere-like CaSO₃:Ce·1/2H₂O which the particle size is 3 to 8 µm. The sphere-like CaSO₃:Ce·1/2H₂O could be reduced to the sphere-like CaS:Ce at moderately low temperatures (350°C and 450°C) in a stream of hydrogen sulfide and in a single firing process. However, the CaS:Ce phosphors prepared at 350°C and 450°C did not show an intense photoluminescence comparable to those prepared at higher temperature. The higher the reduction temperature increased, the higher the relative emission intensity became. This is a probable reason that the higher reduction temperature led to sintering of particles and more perfect crystals. A utility of selection of CaSO₃:Ce·1/2H₂O as a starting material was not recognized with respect to preparation of a higher emission phosphor.

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1 Introduction

Calcium sulfide (CaS) is among the earliest phosphor hosts of cerium for electroluminescent materials. Lehmann and Ryan¹,²) prepared CaS:Ce phosphors by a following twostep reaction; first, unactivated CaS was obtained by firing calcium sulfate in an atmosphere of a mixture of hydrogen and hydrogen sulfide and then the CaS mixed with cerium sulfide, ammonium chloride and sulfur was fired in an argon atmosphere at 1200°C. Vij and Mathur³,⁴) prepared CaS:Ce phosphors by reducing calcium sulfate containing cerous nitrate with carbon in the presence of a large amount of sodium sulfate as a flux at 900°C. In this process, the reduction of calcium sulfate to CaS, and the activation of CaS with cerium were achieved in a single firing process at relatively low temperatures. The phosphors by usage of a large amount of sodium sulfate flux gave the phosphors consisted of well-developed particles about 10 µm in size, having somewhat higher stability in a water slurry. Okamoto and Kato prepared CaS:Ce phosphors by a sulfurizing flux method in a single process⁵,⁶). The phosphors prepared by this method also consisted of well-crystallized, independent particles, large particle size (a few microns to submillimeters), and high luminescence efficiency.

We have carried out extensive investigations on preparation conditions of high emission polycrystalline CaS:Ce phosphors from cerium-contained calcium sulfate dihydrate or calcium sulfate hemihydrate⁷,⁸,⁹) in a single firing process. In this paper, in order to obtain a sphere-like CaS:Ce phosphors, we prepared a sphere-like cerium-contained calcium sulfite hemihydrate (CaSO₃:Ce·1/2H₂O). The temperature dependence of reduction of CaSO₃:Ce·1/2H₂O to CaS:Ce on a particle shape, particle size and emission intensity are reported. Furthermore, an emission intensity of the...
phosphors prepared from CaSO$_3$·Ce·1/2H$_2$O was compared with that of phosphors obtained from calcium sulfate dihydrate or hemihydrate in our previous works$^{7-10}$.

2 Experimental

2.1 Preparation of CaSO$_3$·Ce·1/2H$_2$O and CaS·Ce

All chemicals used were of reagent grade. CaSO$_3$·Ce·1/2H$_2$O were prepared by dropping a 500 ml of 1 mol·dm$^{-3}$ Na$_2$SO$_3$ solution contained a given concentration of cerium sulfate (III) into a 500 ml of 1 mol·dm$^{-3}$ CaCl$_2$ solution while agitating the reaction solution at a speed of about 1000 rpm at 25°C for 30 min. Cerium sulfate (III) was previously dissolved in the Na$_2$SO$_3$ solution. The amount of cerium added was 0.2 mol% against the calcium content in this reaction system. The precipitates were filtered off and rinsed with water, methyl alcohol and diethyl ether in this order.

CaS·Ce phosphors were prepared by reducing the CaSO$_3$·Ce·1/2H$_2$O in a stream of hydrogen sulfide at 300, 350, 450, 600, 800, 900, 1000 and 1100°C, respectively, for 16 hours. After cooling at a constant speed of 2°C/min to room temperature in the same atmosphere, the products were lightly ground to fine powders. They were obtained in a single firing process.

2.2 Measurements

The crystalline phase of the CaSO$_3$·Ce·1/2H$_2$O and the firing products were analyzed by means of a X-ray diffraction method (XRD) using a Rigaku Denki RAD-3C X-ray diffractometer. Particle shapes and size of CaSO$_3$·Ce·1/2H$_2$O and the firing products were observed with a Hitachi S2100 scanning electron microscope operated at 20kV. For photoluminescence measurements, a Shimazu RF-502 fluorophotometer was used. The emission intensities were normalized as compared with equal peak height of a standard CaS·Ce phosphor offered by Mitsui Mining & Smelting Co., Ltd. An emission intensity of the standard phosphor was 74% with respect to a green emitting phosphor ZnS·Cu,Al(P.41).

3 Results and Discussion

3.1 Preparation of CaSO$_3$·Ce·1/2H$_2$O

Different particle shapes of calcium sulfite hemihydrate (CaSO$_3$·1/2H$_2$O) have been prepared by dropping a CaCl$_2$ solution into a Na$_2$SO$_3$ solution$^{11}$, or by passing a stream of SO$_2$ gas through a suspension of Ca(OH)$_2$$^{11,12}$. The CaCl$_2$-Na$_2$SO$_3$ reactions yielded sphere-like particles of 5 µm in average size. The Ca(OH)$_2$-SO$_2$ reactions gave also sphere-like particles (4 to 6 µm in size). In the CaCl$_2$-Na$_2$SO$_3$ system, the particle shape of CaSO$_3$·1/2H$_2$O can be controlled by adjusting reaction conditions, for example, concentration of the reaction solutions, preparation temperature and pH of reaction system. The concentration of the reaction solutions especially affected on the particle shape. Sphere-like particles composed of radially grown needle-like fine particles were obtained with a lower concentration such as 0.5 mol·dm$^{-3}$, and dendrite particles were obtained with a higher concentration such as 2 mol·dm$^{-3}$ for both CaCl$_2$ and Na$_2$SO$_3$ solutons. Aggregates consisted of plate-like fine particles were obtained with a 0.05 mol·dm$^{-3}$ solution.

We tried to prepare CaSO$_3$·Ce·1/2H$_2$O by dropping a 500 ml of 1 mol·dm$^{-3}$ Na$_2$SO$_3$ solution into a 500 ml of 1 mol·dm$^{-3}$ CaCl$_2$ solution with the aim of preparing the sphere-like ones. Figure 1 shows a SEM image of the as-prepared CaSO$_3$·Ce·1/2H$_2$O. This indicates that the dominant particle shapes are sphere-like and the particle size is 3-8 µm. The surface morphology of the CaSO$_3$·Ce·1/2H$_2$O consisted of needle-like and dendrite fine particles. This result was the same as reported by Yasue$^{11}$ or Matsuno$^{12}$. It is considered that the cerium

Fig. 1 SEM image of CaSO$_3$·Ce·1/2H$_2$O as the starting material obtained from the Na$_2$SO$_3$-CaCl$_2$ system.
added in the reaction solution did not affected the resulted particle shapes and surface morphology. The XRD patterns of the starting material which were identified as calcium sulfate hemihydrate (CaSO₃·½H₂O) are shown in Fig. 2. Though CaSO₃·Ce·½H₂O may have oxidized to calcium sulfate dihydrate in the meantime of the precipitation reaction, any crystalline phase of the calcium sulfate dihydrate were not detected.

Thus far it has been hard to prepare a sphere-like starting material; calcium sulfate dihydrate or hemihydrate. However, it was found that it was easy to prepare a sphere-like CaSO₃·Ce·½H₂O by means of CaCl₂-Na₂SO₃ precipitation reaction.

3.2 Reduction temperature dependence

It has been reported¹³) that the thermal decomposition process of CaSO₃·1/2H₂O was complicated and extremely affected by heating in an oxidation or a reduction atmosphere. In the both atmosphere, CaSO₃·1/2H₂O dehydrated to calcium sulfate (CaSO₄) at 350 to 450°C. In the oxidation atmosphere at 450-600°C, CaSO₃ was oxidized to calcium sulfate dihydrate (CaSO₄).

In the our present experiment, the reduction was carried out in a stream of hydrogen sulfide. The reduction temperatures between 300 to 1100°C were chosen. At 300°C, CaSO₃:Ce·1/2H₂O did not reduced to CaS. The XRD patterns of the products obtained at the various reduction temperatures (350, 450, 600 and 900°C) are shown in Fig. 3. These indicate that the crystalline phase of the products obtained at 350, 450 and 900°C were identified as CaS and furthermore any calcium oxide phase was not recognized, but that of the products at 600°C were identified as a mixture of both CaS and CaSO₄. The products obtained at 800°C showed slightly formation of CaSO₄. The XRD patterns of the products obtained at the other temperatures over 1000°C were same as that at 900°C.

In a non-oxidation atmosphere such as a nitrogen or an argon gas, it has been considered that a disproportionation reaction of CaSO₃ to CaS and CaSO₄ occurred at a higher temperature than 650°C¹³), and we recognized the disproportionation reaction in our previous reports where calcium sulfate dihydrate or hemihydrate were reduced at 800°C in a stream of hydrogen gas with or without sulphur. This disproportionation reaction was also observed in the present experiment. Therefore, it was found that, at 600 to 800°C, sole CaS phosphors could not be obtained.

Up to the present, it has been recognized that CaS was generally produced from calcium carbonate or CaSO₄ and that reducing or sulfurizing temperature was higher than at least about 800°C in a stream of either hydrogen gas or nitrogen gas³-⁶). In this experiment, although the production of CaSO₄ are recognized at 600 to 800°C, CaSO₃·Ce·1/2H₂O could also be reduced to CaS:Ce at the other temperatures, for example, as low temperature as 350°C. According to these results, although the disproportionation reaction occurred at 600
to 800°C, it is also realized that CaS phosphors can be prepared by means of reducing CaSO₃:Ce·1/2H₂O at as low as 350°C. On the other hand, at 300°C, CaSO₃:Ce·1/2H₂O was not reduced to CaS by long reaction time of about 30 hours. The formation of CaS at even 350°C was due to the use of CaSO₃:Ce·1/2H₂O as the starting materials. As this reason, CaSO₃:Ce·1/2H₂O dehydrates at 350 to 450°C, so the structure changes of CaSO₃:Ce·1/2H₂O to CaSO₃ occur simultaneously, and then, CaSO₃:Ce·1/2H₂O or CaSO₃:Ce reacts easily with hydrogen sulfide to give CaS.

From above results and our reported works, following things were found. It is hard to prepare a CaS from calcium sulfate dihydrate or hemihydrate at relatively low temperature. It is easy to obtain a CaS from CaSO₃:Ce·1/2H₂O at as low as 350°C. A work that CaS was obtained at such temperature as 350°C has not been reported.

### 3.3 Morphology of CaS:Ce

Figures 4a and 4b show SEM images of CaS:Ce prepared at 350 and 450°C. The morphology obtained at both temperatures represent similar features of the microstructure where sphere-like particles with 3-8 μm in size are observed. A sintered particle was not recognized due to moderately low temperature. Figure 4c shows a SEM image of the products obtained at 600°C. It can be seen that the sphere-like particles were partially sintered to round particles. Although the sintered particles were observed, particle size maintained unchanged. Figure 4d shows a SEM image of the CaS:Ce at 900°C. Independent particles sintered and grew larger. The same result as the appearance of sintering CaS:Ce was able to be also observed in our previous reports.

So far, it is considered that this sintering phenomenon was extremely revealed at over 900°C. Because, sodium was incorporated in

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**Fig. 4** Morphology of the products obtained at various temperatures.

the starting materials at the precipitation process of CaSO₃·Ce¹/₂H₂O, the sodium probably plays a role as a flux like sodium sulfate after all.

3.4 Photoluminescence
The cerium content in CaS:Ce phosphors affects the luminescence intensity. The amount of cerium added was 0.2 mol% against calcium content in the reaction system. The cerium content in the CaSO₃·Ce¹/₂H₂O and the CaS:Ce were determined by means of X-ray fluorescence analysis. The cerium content in the CaSO₃·Ce¹/₂H₂O was 0.2 mol%. A given cerium ion in the Na₂SO₃ solution was incorporated in the CaSO₃·Ce¹/₂H₂O. However, the cerium content in the CaS:Ce was 0.1 mol%. Resulting cerium content for all preparing CaS:Ce was the same value. Figure 5 shows emission spectra of the CaS:Ce at an excitation wavelength of 254 nm and excitation spectra was taken at an emission wavelength of 505 nm. Peaks are observed near 505 nm (emission band I) and 555 nm (emission band II). The emission band I and II correspond to the transitions from a ²T₂g state to ²F₅/₂ and ²F₇/₂ states, respectively. The peak position did not change with temperatures. The excitation spectra was the same pattern as that we have been reported⁰).

Figure 6 shows emission intensity of the CaS:Ce against the reduction temperatures. The emission intensity increased with raising reduction temperatures and saturated at over 900°C. This is because, it can be seen that the higher reduction temperature resulted to the more perfect crystal. This agreed with the SEM data observed as sintering particles. The narrowing of XRD peak width shown in Fig. 3 also supports this reasoning. As the reduction temperature increased, the body color of the products changed from whitish yellow to pale yellow.

It was found that a more perfect crystal of CaS:Ce produced a high emission phosphor. In general, in order to obtain a more perfect crystal of phosphor, a higher temperature is recommended. So, although we selected the CaSO₃·Ce¹/₂H₂O as a starting material and prepared CaS:Ce phosphor at as low as 350°C, a higher temperature was necessary to obtain a high emission CaS:Ce phosphor. Therefore, a merit of selecting a CaSO₃·Ce¹/₂H₂O as a starting material was not recognized with regard to a use of phosphor. It was seen that CaSO₃·Ce¹/₂H₂O behaved like either calcium sulfate dihydrate or hemihydrate with respect to a high emission intensity.

4 Conclusions
We have shown the preparation conditions of CaS:Ce phosphors from cerium incorporated
CaSO$_3$·1/2H$_2$O. Sphere-like CaS:Ce phosphors can be seen from CaSO$_3$:Ce·1/2H$_2$O at as low as 350°C in a stream of hydrogen sulfide and in a single firing process. However, the CaS:Ce phosphors prepared at 350°C did not show intense photoluminescence. The sintering was observed at the higher reduction temperature. The higher the reduction temperature is, the stronger the relative emission intensity becomes. A utility of selection of CaSO$_3$:Ce·1/2H$_2$O as a starting material was not recognized with respect to a higher emission phosphor.

References

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CaSO$_3$ : Ce · 1 / 2 H$_2$OからのCaS : Ce蛍光体の作製条件

松井 博・岡本 裕信*・猪野 浩平*・橋詰 源蔵・足立 吟也**
（兵庫県立工業試験場、*サンエス石窯協、**大阪大学工学部応用化学科）

CaSO$_3$ : Ce · 1 / 2 H$_2$Oから緑色を発光するCaS : Ce蛍光体の作製条件について検討した。CaCl$_2$溶液とNa$_2$SO$_3$溶液との沈殿反応により粒子径が3 ～ 8 μmの球状のCaSO$_3$ : Ce · 1 / 2 H$_2$Oを得た。球状CaSO$_3$ : Ce · 1 / 2 H$_2$Oから硫化水素気流中、比較的低い温度（350°Cと450°C）で球状CaS : Ceを得た。しかしながら、350°Cと450°Cで得たCaS : Ce蛍光体は他の高い温度で作製した蛍光体と比較して強いフォトラミネンスを示さなかった。還元温度が高ければ高いほど発光強度は増加した。これは、より高い温度で還元することにより、粒子の焼きがより完全な結晶が得られたものと思われる。出発物質としてCaSO$_3$ : Ce · 1 / 2 H$_2$Oを選んだ有用性はより高い発光をする蛍光体の観点からみると認めることはできなかった。

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