Preparation of $CaS:Eu^{2+}$ Phosphor by Microwave Heating Method and its Luminescence

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Abstract: This is the first report of using the microwave heating technique to synthesize calcium sulphide activated by europium whose structure is determined as the face-centered cubic by conventional X-ray powder diffraction method. The phosphor has maximum excitation peaks located at 280 nm and 560 nm and the maximum emission of the phosphor is 630 nm. When the concentration of Eu^{2+} in CaS increases from 1.0×10^{-5} to 1.0×10^{-2} mole per mole host, the body colour of the calcium sulphide activated with europium changes from white, through light-red to pink to deep-red. The phosphor obtains the longest afterglow at the concentration of 0.1% Eu^{2+}-doped and is a kind of good material excited by sunlight.

Keywords: Microwave radiation heating, calcium sulphide, europium, luminescence.

Alkaline-earth sulfides have been found to be excellent host materials for the cathodo-, photo-, thermo-, and electro-luminescent phosphors[1-3]. Red-emitting $CaS:Eu^{2+}$ have already been described in the literature[4,5]. In the past, calcium sulphide was mainly prepared by conventional high temperature solid state method through the stream of H_2S and H_2 or CS_2 as sulphurizing and protection atmosphere, which expended quite long reaction time of 2-72 h[6] and consumed a great deal of the sources of energy in vain. We first applied the microwave heating method to prepare the phosphor of calcium sulphide activated by europium and obtained a good result.

All chemicals were of analytical grade except the activator compound , which was high purity (4N). The $CaS:Eu^{2+}$ phosphor was prepared from starting compositions consisting of $CaCO_3$, NH_4X (X=F, Cl), elemental sulphur, and Eu_2O_3 or $Eu(NO_3)_3$. The mole ratio of $CaCO_3$, NH_4X, and elemental sulphur was 1:1:3. The concentration of europium was varied from 0.001 to 1 mol% per mole of $CaCO_3$ by adding Eu_2O_3 or $Eu(NO_3)_3$. The starting compositions were well mixed by an agate mortar and pestle by adding ethyl alcohol. The mixture was placed in a covered alumina crucible and this crucible was placed in a larger covered alumina crucible. The spacing between the crucibles was filled with ferric oxide and active carbon to absorb microwave to heat the mixture and to avoid the oxidation of the products in the heating process. The crucible with chemicals was placed in a home microwave oven to react for about twenty five minutes. Then the product was cooled to room temperature and was washed with cold deionized water. After rinsing with ethyl alcohol, the product was dried at 80℃ for a couple of hours. The final phase was checked with conventional X-ray diffraction technique and the spectra of the phosphor were recorded at room temperature by Hitachi Model MPF–4 Fluorescence Spectrophotometer with 150W xenon lamp.

Heating materials by applying the microwave radiation energy depends on partly the dissipation factor of the materials, *tan*δ, which is defined as the ratio of the dielectric loss (ε”) and the dielectric constant (ε’), *i.e.* $tan\delta = \varepsilon'' / \varepsilon'$, which indicates the ability of materials to convert electromagnetic energy into heat energy at a given frequency and temperature. The dissipation of microwave energy by a material is accomplished through two kinds of mechanisms of dipole molecule rotation and ionic conduction. With the aid of dipole molecule rotation and ionic conduction the molecules bring about fast movement, but the structure of the molecules does not change. By the action of microwave radiation the molecules change promptly from a relatively static state into a dynamic one, that is, after obtaining microwave radiation energy the dipole molecules produce heat effect by molecular rotation at top speed of several hundred million times per second. Because the prompt change from static to dynamic state is occurring within the molecules, the microwave heating is described as ‘inside heating’. We first introduce the microwave absorber—ferric oxide to the preparation of the phosphor of the calcium sulphide activated with europium by microwave heating technique and have achieved success.

Figure 1 The X-ray diffraction pattern of the calcium sulphide activated with europium

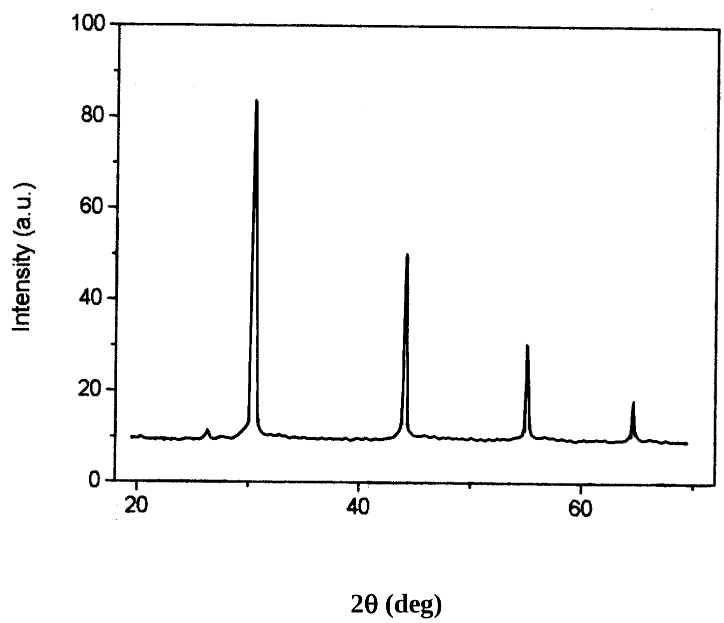
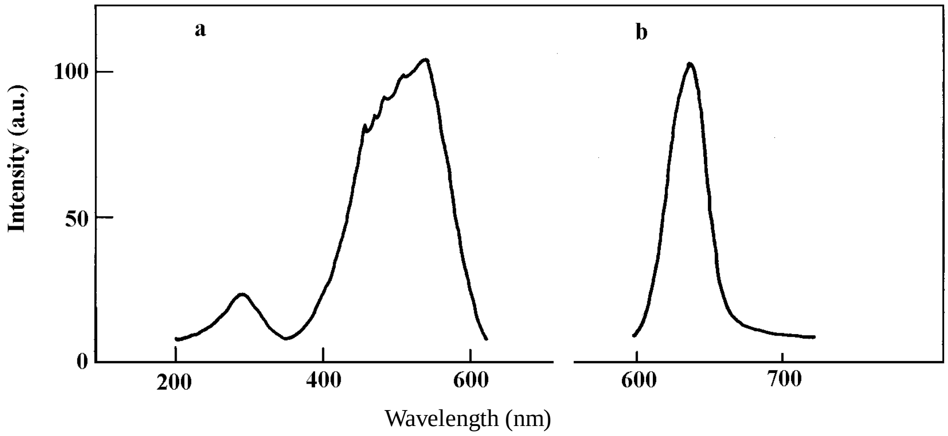


Figure 1 shows the X-ray diffraction pattern of the phosphor. The XRD analysis indicates that the calcium sulphide activated by Eu^{2+} belongs to face-centered cubic symmetry structure. The lattice parameter calculated is 0.5698 nm and is identical compared with the value of ASTM standard card of 0.56948 nm. The excitation and

Figure 2 The excitation (a) and emission (b) spectra of Eu^{2+} in CaS prepared by microwave heating technique



emission spectra of the CaS:Eu^{2+} are shown in **Figure 2**. As seen from **Figure 2**, the excitation of the phosphor consists of two bands, at 280 nm and about 560 nm, and the phosphor has stronger absorption from 400 nm to 600 nm, so the CaS:Eu^{2+} is a good phosphor excited by sunlight. Under the excitation of 280 nm or 560 nm wavelength, the emission wavelength of CaS:Eu^{2+} is 630 nm. The body colour and afterglow of the phosphor CaS:Eu^{2+} varies with the change of doped concentration of Eu^{2+}. The effective afterglow of the phosphor becomes the longest at Eu^{2+} concentration of 0.001 mole per mole host. When the concentration of Eu^{2+} in CaS is less than 10^{-5} mol/mol, the phosphor body color is white. With the increase of the concentration of Eu^{2+} the body colour of the phosphor changes from light - red to pink to bright deep - red. When the

Table 1 The dependence of the doped concentration on the spectra parameters of Eu^{2+} in CaS

Concentration mol/mol host	Excitation /nm	Emission /nm	Half high width /nm	Relative intensity	Body colour
0.00001	558	630	61	65	white
0.00005	558	630	61	70	light-red
0.0001	559	631	61	88	light-red
0.0008	560	631	61	100	pink
0.001	560	632	61	94	pink
0.005	562	634	61	90	deep-red
0.008	563	635	61	80	deep-red
0.01	567	635	61	77	deep-red

concentration of Eu^{2+} in CaS is more than 0.003 mol/mol, the body colour of the phosphor does not change any more. The dependence of the concentration of Eu^{2+} on the spectra parameters of Eu^{2+} is listed in **Table 1**. As shown in **Table 1**, the excitation and emission wavelength of Eu^{2+} shifts to the direction of low energy and the half high width of Eu^{2+} remains constant as increasing the concentration of Eu^{2+} in CaS. The emission strength of Eu^{2+} reaches the maximum at the Eu^{2+}-doped concentration of 0.0008 mole per mole host.

In conclusion, calcium sulfide activated by europium has been prepared by the microwave heating method for the first time. The phosphor has good luminescent properties compared with the conventional solid state preparation. This kind of new synthesis method is reliable, easy in operation with simple equipment, and the reaction speed is enhanced greatly and reaction time is shortened greatly, so it is extremely economized in terms of energy expenditure with the use of the microwave heating method. In our opinion, the microwave heating method has good prospect for the preparation of phosphors whether in laboratory or in industrial production.

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