

Notes

A Novel Single-Source Precursor Route for the Synthesis of Blue-Green Phosphor SrS:Ce³⁺

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Received January 9, 2014, Accepted March 6, 2014

Key Words : Single-source precursor, Lanthanide, Luminescence, SrS:Ce³⁺

A great amount of research on lanthanide-doped alkaline earth sulfides (AES) have been carried out for quite some time because of their versatile optical properties and great potential for technical applications such as optical storage, OSL dosimeters, infrared sensors, image intensifiers, and near-infrared to visible converters.¹⁻⁶ In particular, Ce(III) doped SrS is being given a great importance in recent years because of its bright blue-green emission. SrS:Ce³⁺ phosphor has been widely studied to improve the stability against moisture, luminance, luminous efficiency, etc. and by doping compensator it is expected to give high luminous yield for possible application in cathodoluminescence (CL) and electroluminescence (EL) displays.⁷⁻¹²

In general, alkaline earth sulfide phosphors are prepared by sulfidizing alkaline earth based sulfate, carbonate, etc., at high temperature (> 1000 °C) in N₂ with H₂S or CS₂ atmosphere.¹³⁻¹⁶ However, these methods have the potential danger because both of H₂S and CS₂ are hazardous gas to environment and health. In addition, the SrS:Ce³⁺ phosphor can be obtained by the carbothermal reduction technology of preparation, for example: the powder mixture of stoichiometrical SrSO₄ and Ce(SO₄)₂ fires at 900 °C in a strong carbon reducing atmosphere.^{17,18} The problem of this method is that the reaction produces poisonous gas CO and potentially CS₂. Another route to obtain alkaline earth sulfide phosphors is to reduce alkaline earth sulfate under H₂/N₂ or H₂/Ar atmosphere.¹⁹⁻²¹ The disadvantage of this method is that it generates much of H₂S in the redox reaction, which causes an unreasonable S/M ratio, namely, sulfur-lost problem. The loss of sulfur results in the S vacancies in the AES lattice, accordingly, the lanthanide-doped alkaline earth sulfides phosphors show low quality and luminance. Sometimes, the compensator sulfur is introduced to the reaction system to supply S atoms to the AES lattice,²² however, it can be easily understood that the purity and S/AE ratio of product are also quite unexpected.

In this paper, we report on a novel single-source precursor route to prepare SrS:Ce³⁺ phosphor. This method is facile and environmentally friendly (without hazardous gas), and

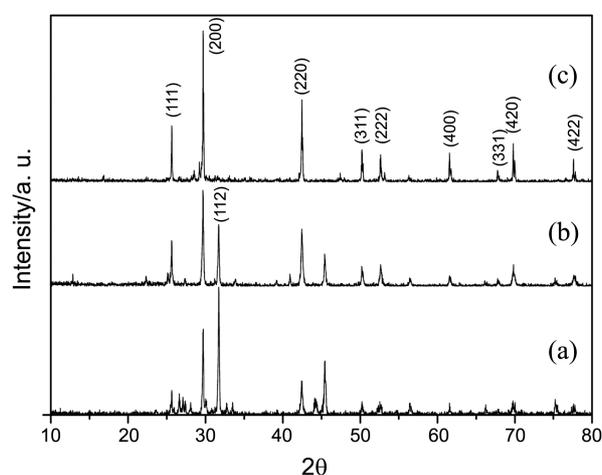


Figure 1. XRD pattern of the SrS:Ce³⁺ obtained at 700 °C (a), 800 °C (b), and 900 °C (c).

the S/Sr ratio of product is reasonable. In addition, the photoluminescent properties of SrS:Ce³⁺ phosphor are also investigated.

Figure 1 represents the XRD pattern of as-synthesized products under thermal treatment at 700 °C, 800 °C, and 900 °C. The lattice of SrS has been formed at 700 °C and 800 °C, but there are impure phases. The XRD pattern of products obtained at 700 °C and 800 °C show two mainly additional peaks at 31.64° and 45.45°, indicating the incomplete reaction at low temperature. In the two peaks, the first one can be attributed to be the reflection 112 of the tetragonal SrS₂ lattice (JCPDS card of 34-0538, space group of *I4mcm*). Up to 900 °C, the SrS lattice was formed entirely. All diffraction peaks of the product obtained at 900 °C can be perfectly indexed by a cubic phase with space group *Fm3m*, which are well matched with the literature data in the JCPDS file 08-0489 (Cubic, a = 6.02 nm). The absence of any other peaks indicates the high purity of products, and the high intensity suggests the formation of SrS lattice in the well crystalline. All these results indicate that under thermal condition, the Sr-S and S-C bonds of molecular precursor break and it

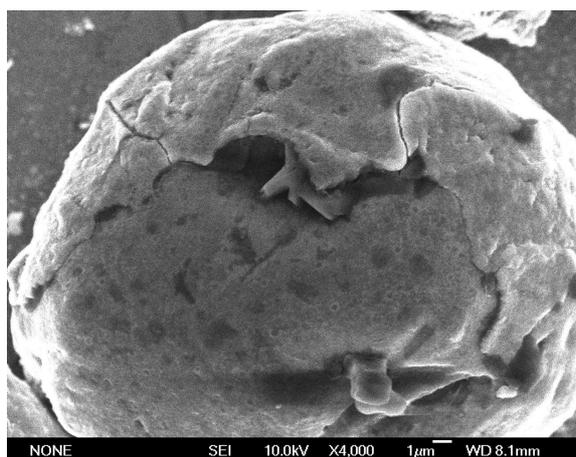


Figure 2. SEM images of SrS:Ce³⁺ prepared at 900 °C.

leads to the formation of SrS₂ or SrS. While at high temperature, SrS₂ tends to be transformed into SrS formation. Figure 2 presents the SEM image of the samples prepared at 900 °C, the obtained phosphors are all spherical and the size of particles ranges from submicrometer to micrometer scale.

According to the results of XRD pattern, the SrS lattice was gradually formed by the decomposition of DDTC complex, and this is significant for the SrS:Ce³⁺ phosphor. In above motioned traditional reduction routes, alkaline earth sulfates (AESO₄) are usually used as precursors and reducers are mostly C or H₂. The redox reaction between reducer and S⁶⁺ cation generates CS₂ or H₂S by-products resulting in a low S/AE ratio of AES lattice since the original S/AE ratio is 1:1, and the loss of sulfur reduces the quality and luminance of products. For this single-source molecular precursor method, the precursor is AE(DDTC)₂ complex, and the S/AE mole ratio is 4:1 in the structure, the excessive sulfur can avoid the loss of sulfur to assure stoichiometry. In addition, it's more important that SrS lattice was formed by a gradual thermal decomposition process, and SrS lattice is not decomposed at 900 °C (the decomposition temperature of SrS is more than 1600 °C), so it can be predicted that the phosphors prepared from AE(DDTC)₂ precursors should have a reasonable value of S/Sr ratio. In this work, the S/Sr ratio of SrS:Ce³⁺ phosphor obtained at 900 °C was measured by a simple method. The phosphors of 0.8614 g, 1.0391 g, 1.2172 g were fired in air at high temperature resulting in product (SrO/CeO₂) of 0.7306 g, 0.8922 g, 1.0647 g respectively, and the S/AE ratio can be calculated to be about 52:48 (used M_{Sr} = 87.62, M_{Ce} = 140.13, M_S = 32.08, M_O = 16).

Another important feature of this single-source precursor method is that the excessive negative valence S can provide a reducing atmosphere, and then prevent the oxidation of Ce³⁺. It possesses universal significance and convenience for the synthesis of low-valent lanthanide ions doped AES phosphors.

In addition, no hazardous gas was used or generated in the preparation course, it's quite environmentally friendly. In the traditional sulfidization method, H₂S or CS₂ are used; in the reduction methods, H₂ is used and CO, H₂S and CS₂ are

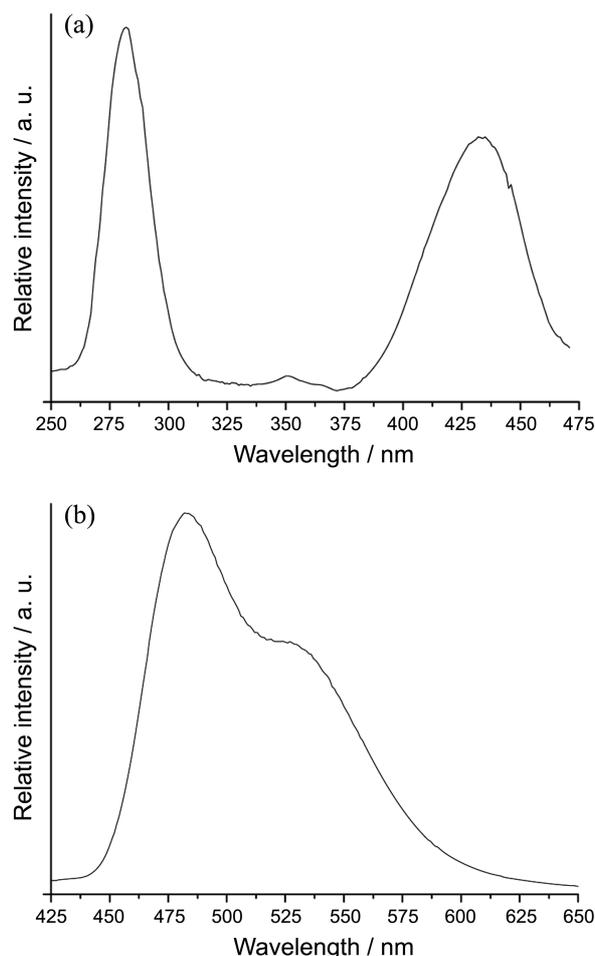


Figure 3. The excitation (left) and emission (right) spectra of SrS:Ce³⁺ prepared at 900 °C.

potentially generated. These gases are hazardous or harmful to body, safety and environment. For this single-source precursor method, the decomposition reaction is performed under N₂ only, which is a green-gas.

It also should be noted is that during the preparation of intermediate complex, a small amount of NaCl resides in the system, and it can act as the charge compensator and then enhance the luminescent intensity of SrS:Ce³⁺ phosphor.¹⁷

The excitation spectrum of SrS:Ce³⁺ phosphor prepared at 900 °C at room temperature shows two main excitation peaks 281 and 432 nm., as shown in Figure 3. The peak at 281 nm is due to the band-to-band transition in the SrS lattice, since the band gap energy of the SrS lattice is about 4.3 eV which corresponds to about 288 nm. The peak at 432 nm is assigned to the 5d crystal field splitting levels corresponding to T_{2g}-Γ₇, and a slight shoulder at 445 nm corresponding to T_{2g}-Γ₈, which can be explained as follow: the Ce³⁺ ion (4f¹) has only one 4f electron, and the low-energy spectroscopy of the ion in SrS lattice is dominated by 4f→5d transition, consequently the excited configuration is 5d¹. In addition, SrS has a rock-salt structure with an O_h site symmetry at the Sr site, so Ce³⁺ has an octahedral coordination configuration when the ion replace Sr, accordingly both the

ground state and excited state of Ce^{3+} are affected by crystal field. The $4f$ -derived levels are dominated by spin-orbit coupling, splitting into ${}^2F_{7/2}$ and ${}^2F_{5/2}$ levels. These are further split into five components by the crystal field. The $5d$ orbitals are split into ${}^2T_{2g}$ and ${}^2E_{2g}$ terms by the crystal field, and are further by spin-orbit coupling. It should be noted that the higher-lying e_g set of $5d$ orbitals is in the conduction band in SrS lattice, so only the position of the lower t_{2g} set is of interest.

The emission spectrum was taken by exciting the phosphor at 281 nm. The emission occurs from the crystal field component of the $5d^1$ configuration to the two levels of the ground state, and trivalent cerium ions produce two emission bands: one prominent peak at 483 nm (blue emission) and the other shoulder peak around 530 nm (green emission), which are attributed to be the characteristic emission ${}^2T_{2g} \rightarrow {}^2F_j$ ($j = 7/2, 5/2$) transition of Ce^{3+} ions.

In summary, the single-source precursor route was utilized to prepare lanthanide-doped alkaline earth sulfide phosphors. Compared with other reported technologies, the molecular precursor method shows several significant superiorities: 1. facility; 2. environmentally friendly; 3. reasonable S/Sr ratio; 4. providing reducing atmosphere itself to prevent the oxidation of low-valent lanthanide ions.

Experimental

Preparation of $\text{SrS}:\text{Ce}^{3+}$ phosphor. In a typical synthesis, 99 mol % of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and 1 mol % of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 95% ethanol, and the solution was stirred for 2 h to form a homogeneous solution. Then another Na-DDTC (DDTC = *N,N*-diethyldithiocarbamate) ethanol solution (the DDTC/ Sr^{2+} ratio was 2:1 with a slight excess of ligand) was added slowly to the metal salt solution under stirring condition. The stirring of the resultant solution was continued for another 2 h (the solution was concentrated by solvent evaporation), which resulted in precipitation of the yellow colored $\text{Sr}_{0.99}\text{Ce}_{0.01}\text{-DDTC}_2$ complex. The precipitate of product was filtered and then dried at 40 °C for 6 h. The solid was then fired in a tube furnace at 700 °C, 800 °C, and 900 °C for 3 h under N_2 atmosphere.

Measurements and Apparatus. The X-ray powder diffraction (XRD) patterns of all samples were performed on a Bruker/D8-Advance with $\text{CuK}\alpha$ radiation ($\lambda = 1.540 \text{ \AA}$). The

luminescence (excitation and emission) spectra for the solid sample were determined with a Perkin-Elmer LS-55 spectrophotometer, whole excitation and emission slit width were 10 and 5 nm, respectively.

Supporting Information. IR spectrum of the intermediate complex is given.

Acknowledgments. Publication cost of this paper was supported by the Korean Chemical Society.

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