

Synthesis and luminescence of Sr_2CeO_4 superfine particles by citrate-gel method

Xibin Yu*, XiangHong He, ShiPing Yang, Xiaofei Yang, Xialin Xu

Department of Chemistry, Shanghai Normal University, Shanghai 200234, PR China

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Abstract

A strong blue-white emission phosphor Sr_2CeO_4 superfine particles, containing SrCe_4O_7 , have been synthesized using a citrate-gel method. The crystalline phase and luminescence properties of superfine particles are reported. The results show that the strong blue-white emission is assigned to $\text{Ce}^{4+}-\text{O}^{2-}$ charge-transfer transition (CTT) of Sr_2CeO_4 and is not related to a lattice defect. The emission spectrum of post-heat-treated particles exhibits a broad band maximum at 470 nm, and the emission intensity is not affected by the existence of SrCe_4O_7 .

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1. Introduction

Rare-earth ions can be almost used to design unlimited new luminescent material because of its special 4f energy level transition. Eu-doped Y_2O_3 [1,2] and silicate [3,4] are the most typical luminescent materials of the rare earth with extensive application. Recently, a new rare-earth luminescent material Sr_2CeO_4 , possessing one-dimensional chains of edge-sharing CeO_6 octahedron, has been synthesized successfully and identified through combinatorial technique, and its luminescence primarily is originated from charge-transfer transition (CTT) [5,6]. This material emits blue-white fluorescence by excitation through the X-ray, cathode ray and ultraviolet ray [5–9]. In addition, it owns the characteristic broad band to take the absorption, which can be used as the matrix material when suitable doped ion is selected [10].

To date, the methods of preparing Sr_2CeO_4 have conventional high-temperature solid-state method [5,6,11], chemical coprecipitation [7,12] and ultrasonic spray pyrolysis technique [13]. Solid-state method demands 1000 °C above temperature and long-time post-heat treatment, in which Sr_2CeO_4 forms large-size particles with low surface area and is easily contaminated by impurities. The sintered

temperature of the coprecipitate method also is very high (1100 °C), with the chemical wastewater of great capacity depleting. The ultrasonic spray pyrolysis techniques are too expensive and complicated to be popularized in an ordinary laboratory. In this paper, the citrate-gel method is used to prepare the Sr_2CeO_4 superfine particles with $\text{Sr}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3$ and citrate acid as the starting materials. The method shows the character of a lower reaction temperature and short reaction time. The resultant starts crystallization at 700 °C and can obtain Sr_2CeO_4 superfine particles with good crystals involving SrCe_4O_7 phase at 850 °C. The mean particle size of as-prepared Sr_2CeO_4 is about 60 nm and emits stronger blue-white luminescence than that of the solid-state method.

2. Experimental

The starting solution is prepared by dissolving $\text{Sr}(\text{NO}_3)_2$ (AR) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR) (molar ratio of Sr/Ce is 2:1) in distilled water under stirring and heating. Then, citric acid monohydrate (AR) is dissolved in the above solution as the chelating agent, and the resultant mixture is stirred at 75–80 °C for 3 h. A slight yellow transparent gel is obtained after concentrating the solution by slow evaporation. The yellow drying gel is obtained under drying at 110 °C, and these drying gel is finely grounded in agate mortar and fired at

* Corresponding author. Tel.: +86-21-64324528; fax: +86-21-64322511.

E-mail address: xibinyu@shtu.edu.cn (X. Yu).

various temperatures from 700 to 1000 °C for 2 h in muffle furnace in air. Finally, the Sr₂CeO₄ superfine particles are obtained.

The Sr₂CeO₄ is also prepared according to a conventional solid-state reaction method [5]. Strontium carbonate (AR) and cerium oxide (AR) are used as starting materials. These starting raw substances are thoroughly homogenized in acetone using an agent mortar and pestle, dried, and sintered in a flow of dried air at 1000 °C for 6 h.

X-ray diffraction patterns are recorded with a Rigaku D/MaxIII B X-ray diffraction (XRD) using Cu/K α radiation, 40 kV, 50 mA. The excitation and emission spectra are recorded using VARAIN Cary-Eclipse 500 spectrofluorometer equipped with an 80-W xenon lamp as excitation source. All the measurements are performed at room temperature.

3. Results and discussion

The XRD patterns for Sr₂CeO₄ superfine particles as prepared at various temperatures are shown in Fig. 1. JCPDS date files nos. 22-1422, 25-0746, 27-1304, 34-0394, 15-0305, 23-1412, and 22-1423 are used to identify Sr₂CeO₄, Sr(NO₃)₂, SrO, CeO₂, Sr, SrCeO₃, and Ce₄SrO₇, respectively. The results show the presence of Sr, Sr(NO₃)₂, SrO, SrCeO₃ and CeO₂ phase in the particles as prepared at 700 °C, and no diffraction peak of Sr₂CeO₄ phase is observed for the sample sintered at this temperature, indicating that the Sr₂CeO₄ phase is not formed under 700 °C. Metal Sr is formed due to the reduction of decomposing citrate acid in the atmosphere. Although the Sr₂CeO₄ phase is dominant in the sample sintered at 850 °C and a little Ce₄SrO₇ is also observed, the pure Sr₂CeO₄ phase does not form even at 1000 °C. The particles as prepared at 1000 °C still contain Sr₂CeO₄ and Ce₄SrO₇ phase. The crystallinity of the particles is improved by increasing the temperature, which can be tested through the change in full width at half maximum (FWHM). At the same time, the diffraction peak intensity of Ce₄SrO₇ phase at $2\theta = 39.6^\circ$ is also improved by

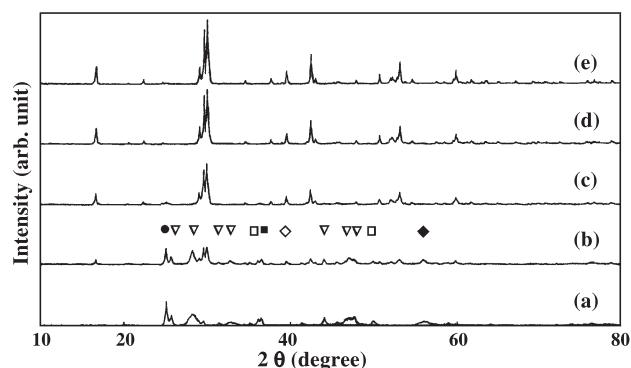


Fig. 1. The XRD patterns of Sr₂CeO₄ superfine particles sintered at various temperatures: (a) 700, (b) 800, (c) 850, (d) 900 and (e) 1000 °C; (●): Sr; (▽): Sr(NO₃)₂; (□): SrO; (■): SrCeO₃; (◇): Ce₄SrO₇; (◆): CeO₂.

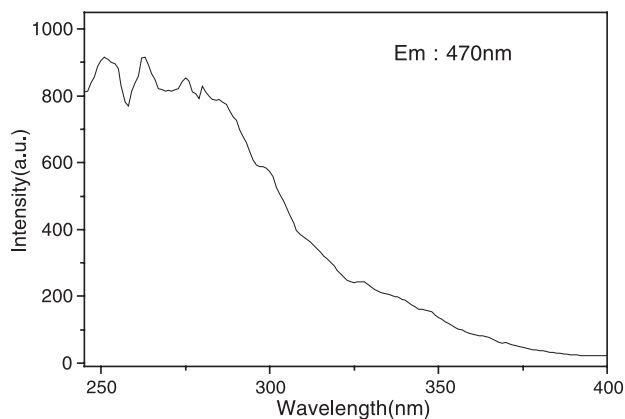


Fig. 2. Excitation spectrum for Sr₂CeO₄ superfine particles.

increasing the temperature from 850 to 1000 °C. The other intermediate products are inverted into the resultant in this temperature range. In the citrate-gel process, the mean size of the particles is about 60 nm (this value is from the Scherrer equation $D = 0.9\lambda/\beta\cos\theta$, where D is the crystal size of the particles, λ is the wavelength of the light, β is the full width in radiation at half maximum of the peak, and θ is the Bragg angle of the X-ray diffraction peak) and can be easily controlled by changing the concentrations of the starting solution. As a result, it is elucidated that Sr₂CeO₄ superfine particles (contain less Ce₄SrO₇ phase) can be synthesized by citrate-gel method in a mild condition.

The emission and excitation spectrum of Sr₂CeO₄ superfine particles at room temperature with various post-heat treatment temperature are shown in Figs. 2 and 3, respectively. The luminescent characteristics of the particles depend on its size and other properties including the degree of crystallization, defects and the valence state of the doped activator ions. A broad strong blue-white emission band is observed with a maximum at 470 nm with the full width at half maximum (190 nm). At the same time, a weak peak at 423 nm is noticed. The excitation spectrum shows a broad band with maximum at 255, 262, 274, and 285 nm, respectively, and two shoulder peaks at 300 and 325 nm with a long-tailing absorption stretching to 400 nm. The Stokes Shift is about 9500 cm⁻¹, which is determined from the difference between the first excitation (in this case, at 325 nm) and the emission maximum (470 nm).

According to the JCPDS, the structure of Sr₂CeO₄ is triclinic. However, Danleson et al. [5] reported that Sr₂CeO₄ has an orthorhombic structure and contains one-dimensional chains of edge-sharing CeO₆ octahedron. The luminescent mechanism of this phosphor is based on ligand-to-metal CTT from O²⁻ to Ce⁴⁺ [5,6,9] and not arising from Ce³⁺ defect centers. This charge transfer results in the lower coordination number terminal O atoms associated with the low-dimensional structure in combination with an adjacent Ce⁴⁺ center [5]. In Sr₂CeO₄, there are two different Ce⁴⁺-O²⁻ bond lengths in the lattice [5]. The two excitation peaks at 300 and 325 nm and the emission peaks at 470 nm

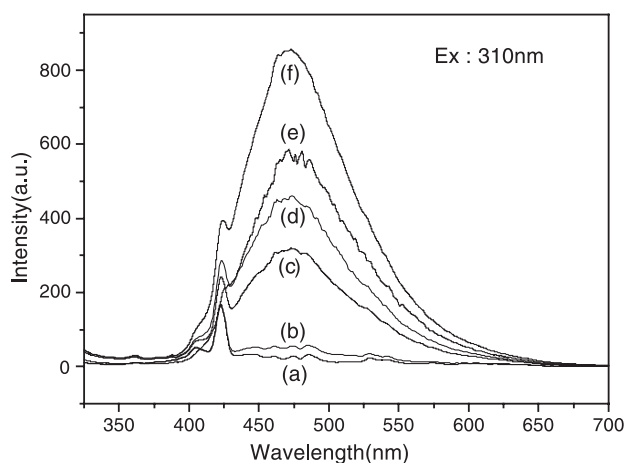


Fig. 3. Emission spectra of Sr_2CeO_4 superfine particles obtained by citrate-gel method: (a) 700, (b) 800, (c) 850, (d) 900 and (f) 1000 °C and (e) solid-state reaction process, 1000 °C.

are observed, which are thus attributed to the different $\text{Ce}^{4+}-\text{O}^{2-}$ CTT. These results match with the structure of Sr_2CeO_4 in solid state. In principle, one can also observe charge-transfer emission at different energies for different $\text{Ce}^{4+}-\text{O}^{2-}$ distances. However, in the CTT, the complex relaxes to the lowest energy excited state. This process is faster than radiative decay from a higher energy excited state [6]. As a result, only an emission peak from the lowest charge-transfer transition is observed.

On the other hand, as is shown in the XRD figure, there exists Ce_4SrO_7 secondary phase in the superfine particles post-heat treatment at above 800 °C. In Ce_4SrO_7 , the Ce ion is in the +3 oxide state and Ce^{3+} has only one 4f electron ($4f^1$). The lowest 5d energy level of Ce^{3+} in Sr_2CeO_4 matrix will be split into several sub-energy levels, which will result in the presence of more than one excitation band. Thus, we may come to a conclusion that four excitation peaks, 255, 262, 274, and 285 nm, occur, which are assigned to the transitions of Ce^{3+} from ground state to its various splitting levels of 5d, respectively. The emission spectra at 423 nm should also be the d–f transition of the Ce^{3+} in Sr_2CeO_4 lattice. At the same time, the presence of Ce_4SrO_7 phase does not affect the emission intensity of Sr_2CeO_4 phosphor.

The intensity of luminescence in as-prepared particles increases obviously with increasing post-heat treatment temperature up to 1000 °C. The intensity of luminescence, reaching the maximum at 1000 °C, is 1.5 times higher than that of the conventional solid-state reaction method. This is because higher post-heat treatment temperature yields better crystallinity and may be related to removal of some luminescence quenching centers (defects in lattice). In the case of the particle post-heat treatment blown to 1000 °C, the low luminescence intensity is attributed to insufficient crystalli-

zation of the particles and defects in the lattice. The decrease in luminescence intensity of the particles above 1100 °C is probably related to decomposition [6] and hard agglomerate of Sr_2CeO_4 . For the particles, this hard agglomerate yields a low density, which causes a strong light scattering.

4. Conclusions

The superfine particles of Sr_2CeO_4 containing Ce_4SrO_7 are successfully prepared by citrate-gel method. The Sr_2CeO_4 crystallites are superfine and low-agglomerated powder. The average size of the superfine particles is about 60 nm. The emission and excitation spectra of the superfine particles show that the broad bands come from the charge-transfer transition of the Sr_2CeO_4 and the d–f energy level transition of the Ce_4SrO_7 , respectively. The emission intensity of photoluminescence at room temperature increases with the post-heat-treatment temperature from 700 to 1000 °C. The presence of Ce_4SrO_7 phase does not affect the emission intensity of Sr_2CeO_4 phosphor. The lattice defects of the superfine particles as prepared by citrate-gel method, for example, oxygen vacancy, are not responsible for the emission. The strong blue-white luminescence mainly involved the charge-transfer transition of Sr_2CeO_4 shows that this superfine particle phosphor has good potential for application as a blue phosphor material and matrix in lamps and field emission displays.

Acknowledgements

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