

MORPHOLOGICAL STUDY OF Sr₂CeO₄ BLUE PHOSPHOR WITH FINE PARTICLES

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Morphological and spectroscopic studies of Sr₂CeO₄ blue phosphor in the form of fine particles prepared from a powdered multi-component precursor, via a combustion method, are reported. Samples were also prepared through a solid-state reaction and from a polymeric precursor for comparison. Citric acid or glycine as fuels in the combustion method lead to a mixture which is heated at 950 °C for 4 h, resulting in spheroidal particles with a diameter between 250-550 nm. Samples from the polymeric precursor result in spheroidal particles (350-550 nm) and from the solid-state reaction in irregular particles (~ 5 µm). Therefore, the combustion method is adequate for preparation of Sr₂CeO₄ in the form of spherical fine particles.

Keywords: blue phosphor; combustion method; fine spheroidal particles.

INTRODUCTION

The search for blue phosphor emitters has been increasing due to their applicability in many fields, such as cathode ray tubes (CRTs), projection televisions (PTVs), fluorescent tubes, X-ray detectors and field emission displays (FED)¹. Very satisfactory red and green commercial materials are being produced, but comparable materials for the blue emission are still lacking and are under development for practical applications²⁻³. Even in the paper industry, fluorescent dyes that absorb UV and emit in blue color are widely used as organic optical brightening agents (OBA) and new inorganic ones have been under investigation⁴. Concerning many of these applications, such as FED and OBA, the availability of systems consisting of uniform particles in size and shape⁵ is also an essential prerequisite for improved performance, and new synthetic routes are being developed in order to reach these systems. Recently, a new promising blue phosphor, Sr₂CeO₄, was developed by combinatorial synthesis⁶ and prepared by different routes, such as conventional solid state reaction⁷, chemical coprecipitation⁸⁻⁹, microwave calcination and pulsed laser deposition¹⁰, polymeric precursors¹¹ and ultrasonic spray pyrolysis¹² methods. From Rietveld refinement data⁹, it was established that the Sr₂CeO₄ structure consists of one-dimensional chain of edge-sharing CeO₆ octahedra that are linked together by Sr²⁺ ions. So, it has an orthorhombic unit cell type, the cerium ions occupy the site symmetry 2/m (C_{2h}), while the strontium and oxygen atoms are located on mirror planes.

In this work, fine particles of the blue phosphor Sr₂CeO₄ are prepared from a powder multi-component precursor via combustion method and a morphological study is reported. Samples prepared by solid-state reaction from raw reagents, as well as using polymeric precursor, were also performed for comparison.

EXPERIMENTAL PART

Analytical grade strontium nitrate (Acros Organics), cerium(III) nitrate solution (obtained from CeO₂ Aldrich 99.999% + HNO₃ Synth P.A. - ASC) and glycine (15527 - Riedel de Haën) or citric acid (P.A. - Synth) as fuels were mixed in a 3:5 molar ratio of nitrate:glycine or 3:2 of nitrate: citric acid to form the precursor solutions, based on

rare earth oxide combustion synthesis¹³. The precursor solutions were concentrated by heating it in a porcelain crucible until excess free water evaporated and spontaneous ignition occurred, resulting in fine powder product, which was grounded. Based on thermal analysis as well as X-ray diffraction studies just reported¹⁴, the conditions of thermal treatment of the powdered multi-component precursors from combustion synthesis were established as being 950 °C during 4 h in order to result in Sr₂CeO₄ as single phase. Sr₂CeO₄ was also prepared from a stoichiometric mixture of SrCO₃ (Aldrich, grade reagent) and CeO₂ (Aldrich, 99.999%) fired at 1000 °C, 4 h, and from polymeric precursor heated at 1100 °C during 4 h, as described in a previous paper¹¹.

All products were characterized by X-ray diffractometry, XRD (SIEMENS D5000 diffractometer, K α Cu radiation, λ = 1,5418 Å, graphite monochromator), luminescence spectroscopy (FLUOROLOG3 ISA/Jobin-Yvon spectrofluorimeter, 450 W ozone free Xenon lamp, Hamamatsu R928P photomultiplier) and scanning electron microscopy, SEM (Zeiss D5M960 microscopy).

Samples for SEM were first dispersed in isopropanol and dropped over a metallic holder, which was coated with a gold film in a controlled deposition by using a Sputter Coater Baltec SCD 050.

RESULTS AND DISCUSSION

X-ray Diffractometry (XRD)

X-ray diffractograms for all samples prepared using different methods are shown in Figure 1. Throughout X-ray pattern sample analyses and comparison with literature data^{8,15} it is possible to verify that in all cases the majority phase found is the luminescent cerate, Sr₂CeO₄. However, samples from solid-state reaction, Figure 1a, have some reflection peaks that can be assigned to the presence of SrCeO₃ and SrCO₃ as impurities. Strontium cerate from polymeric precursor, Figure 1b, only shows SrCeO₃ as secondary phase, considering the detection limits of this technique. This may indicate that heating temperature or residence time, in the solid-state reaction (1000 °C, 4 h) and from polymeric precursor (1100 °C, 4 h), was not enough to obtain the single phase Sr₂CeO₄. On the other hand, when multi-component precursor from combustion method by using glycine or citric acid as fuels is employed, Sr₂CeO₄ is obtained as single phase

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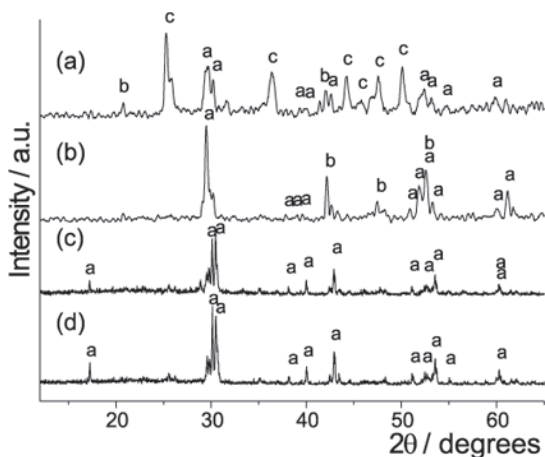


Figure 1. XRD patterns recorded for Sr_2CeO_4 prepared from (a) SrCO_3 and CeO_2 fired at $1000\text{ }^\circ\text{C}$, 4 h; (b) polymeric precursor heated at $1100\text{ }^\circ\text{C}$, 4 h¹¹; precursor from combustion method by using (c) citric acid or (d) glycine as fuels, heated at $950\text{ }^\circ\text{C}$, 4 h. a = Sr_2CeO_4 ⁸, b = SrCeO_3 , PDF n. 83-1156¹⁵, c = SrCO_3 , PDF n.71-2393¹⁵

at lower temperature ($950\text{ }^\circ\text{C}$) during the same heating time (4 h), Figure 1c-d, than those needed to the solid state reaction or polymeric precursor. The different fuels used during combustion method seem do not affect the cerate luminescent phase formation.

Luminescence Spectroscopy in the UV-visible region and Scanning Electron Microscopy (SEM)

All oxysalt samples prepared by using different methods show a white-blue emission under UV excitation, which is characteristic for Sr_2CeO_4 phase. The excitation and emission spectra of all samples are shown in Figures 2 and 3, respectively. Both spectra were measured at room and liquid nitrogen temperatures. For all prepared cerates, a broad excitation band assigned to the charge transfer $\text{O}^{2-}\text{-Ce}^{4+}$ with two maxima¹⁶ around 290 and 340 nm (room temperature) and 280 and

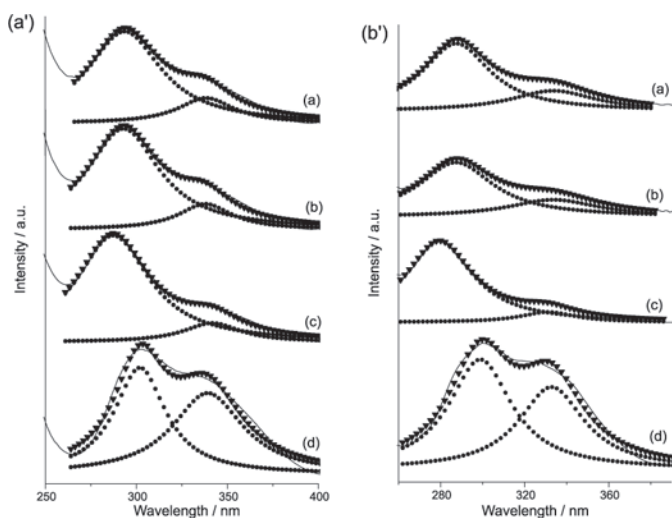


Figure 2. Excitation spectra, $\lambda_{em} = 482\text{ nm}$, (a') at room and (b') liquid N_2 temperatures of Sr_2CeO_4 prepared from combustion method by using (a) glycine or (b) citric acid as fuels, $950\text{ }^\circ\text{C}$, 4 h; (c) polymeric precursor heated at $1100\text{ }^\circ\text{C}$, 4 h¹¹; (d) SrCO_3 and CeO_2 fired at $1000\text{ }^\circ\text{C}$, 4 h. Straight line states for experimental data, small dashed line states for decomposed bands using Lorentz model and up-triangles state for the entirely calculated curve by using Lorentz model and shows the accuracy of the modeling

330 nm (liquid nitrogen) are observed. In the emission spectra, Figure 3, only one band with maximum at 480 nm is detected for all cerate samples at 300 K and 465 nm for all the samples at 77 K.

From SEM results, shown in Figure 4, it is possible to observe that samples from combustion method, independently on the employed fuel, presents spheroidal uniform particles with diameter between 250-550 nm. Sample from polymeric precursor results in Sr_2CeO_4 with spheroidal particles, size between 350-550 nm. On the other hand, sample from solid-state reaction results in Sr_2CeO_4 with irregular particles and average size of 5 μm or greater.

In the excitation spectra, Figure 2, the appearance of two maxima must be related to Ce^{4+} occupying different sites. So, in Figure 2, it is included a decomposition of the detected bands by using a Lorentz model in order to facilitate the comparison between them. It is possible to observe at low temperature a narrowing of the bands and a shifting to higher energy positions due to smaller vibrational energy

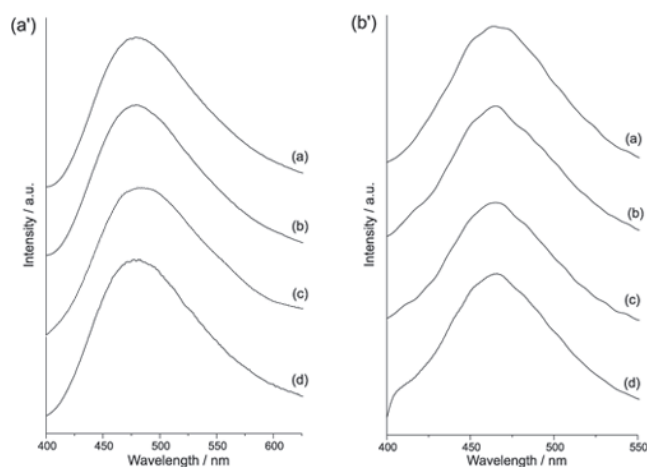


Figure 3. Emission spectra, $\lambda_{ex} = 295\text{ nm}$, (a') at room and (b') liquid N_2 temperatures of Sr_2CeO_4 prepared from combustion method by using (a) glycine or (b) citric acid as fuels, $950\text{ }^\circ\text{C}$, 4 h; (c) polymeric precursor heated at $1100\text{ }^\circ\text{C}$, 4 h¹¹; (d) SrCO_3 and CeO_2 fired at $1000\text{ }^\circ\text{C}$, 4 h

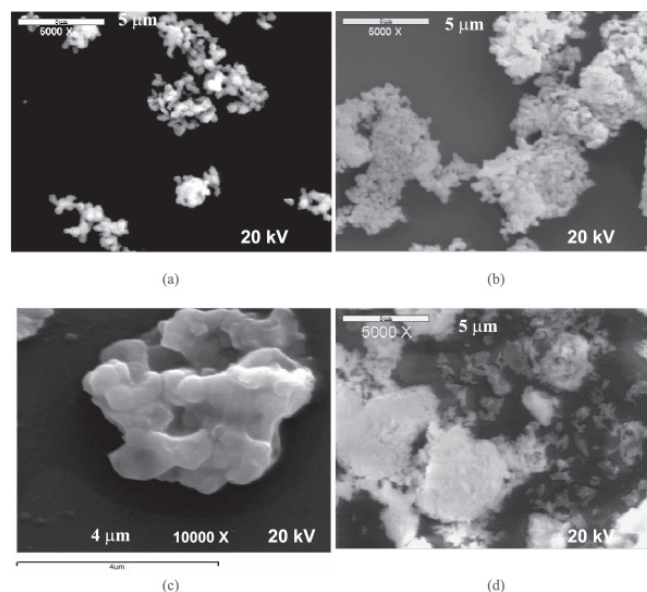


Figure 4. SEM of Sr_2CeO_4 prepared from combustion method by using (a) glycine or (b) citric acid as fuels, $950\text{ }^\circ\text{C}$, 4 h; (c) polymeric precursor heated at $1100\text{ }^\circ\text{C}$, 4 h¹¹; (d) SrCO_3 and CeO_2 fired at $1000\text{ }^\circ\text{C}$, 4 h

contribution. It is also relevant to emphasize that in the case of cerate from solid state precursor, Figure 2d, its excitation band, at 300 and 77 K, is shifted to visible region when compared to the others. Moreover, it is possible to verify that considering the relative intensity between the bands with maximum at lower and higher energy positions, in the case of sample from solid state precursor, the band around 340 nm shows the highest relative intensity compared to the others samples. This behavior must be related to the presence of phase impurities discussed in XRD data section, such as SrCO_3 , which is not detected in the other samples. Carbonate ion must associates with the oxygen atoms at the linear CeO_6 chain in the cerate structure. According to Danielson et al.⁹, the cerium ions are octahedrally coordinated by two types of oxygen atoms, O1 and O2. The symmetry related position of oxygen atom O2 provide four binding sites while the remaining two are satisfied by symmetry related O1 atoms. The O2 oxygen atoms are also involved in linking the unit cell-translated cerium atoms along the c-direction, given linear chains of cerium octahedral parallel to the [001] direction. The Ce-O1 and Ce-O2 bond lengths were reported as 2.201(5) and 2.308(3) Å, respectively⁹, so these two bond lengths gives rise two charge transfer band positions, as mentioned before. If carbonate ion interacts with both oxygen atoms, O1 and O2, Ce-O1 and Ce-O2 bond lengths are affected and consequently the energy of charge transfer bands $\text{O}^{2-}\text{-Ce}^{4+}$. Therefore, the influence of carbonate impurity can shift both observed excitation maxima to lower energy in cerate sample from solid-state reaction, and also must be affecting much more the charge transfer band around 340 nm related to Ce-O2 site.

Luminescence kinetic measurements at 300 and 77 K were also performed, Figure 5a' and b', respectively. The lifetime values calculated from decay curves are listed in Table 1, which are in agreement with Meijerink¹⁶. The long lifetime observed for all

samples can be explained considering the transition as spin-forbidden one. However, when kinetic measurements are taken at 77 K, lifetime curves for all samples (Figure 5b') became similar due to the decreasing on non-radiative relaxation processes. Sample from solid-state reaction shows the higher lifetime value, the ones from combustion method the smallest lifetime and from polymeric precursor an intermediate value. Therefore, the increasing on lifetime, consequently the increasing on non-radiative relaxation process, must also be related to the presence of impurity phases. Sample from solid-state reaction presents both strontium carbonate and non-luminescent cerate phase as impurities and the one from polymeric precursor only the non-luminescent cerate phase.

CONCLUSIONS

Sr_2CeO_4 can be obtained as single phase at lower temperature (950 °C) and shorter time (4 h) by combustion method, using glycine or citric acid as fuel, than those needed to the solid state reaction or polymeric precursor. The combustion method provides blue cerate samples with spheroidal fine particles. Therefore, combustion method is adequate for preparation of blue phosphor using citric acid or glycine as fuel, due to smallest particles size obtained in comparison to the others methods. Moreover, combustion method also provides a cerate with higher purity phase than the others methods. The presense of impurities, in special carbonate phase, seems to affect the luminescent properties of blue phosphor Sr_2CeO_4 , due to the observed changes in the charge transfer bands, which are more pronounced in the CT at 340 nm, related to Ce-O2 site. Lifetime measurement results also corroborate for this conclusion, indicating that the presence of impurities causes an increasing on non-radiative relaxation process, increasing lifetime values.

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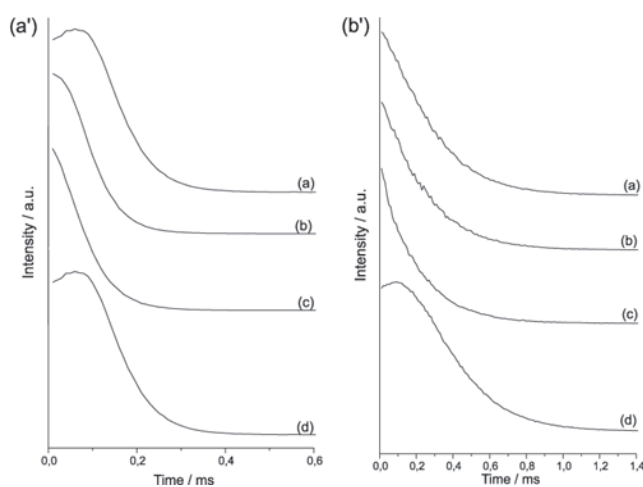


Figure 5. Decay curves (a') at room and (b') liquid N_2 temperatures of Sr_2CeO_4 prepared from combustion method by using (a) glycine or (b) citric acid as fuels, 950 °C, 4 h; (c) polymeric precursor heated at 1100 °C, 4 h¹¹; (d) SrCO_3 and CeO_2 fired at 1000 °C, 4 h

Table 1. Lifetime values of Sr_2CeO_4 prepared from different methods

Temperature (K)	Lifetime (μs)			
	Glycine	Citric Acid	Pechini	Solid State
300	40	46	51	55
77	208	207	207	205