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The blue phosphor Sr_2CeO_4 synthesized by Pechini's method

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Abstract

Blue emitters are very attractive research subjects because of their possible industrial applications as phosphors for field emission displays. Recently, a blue phosphor, Sr_2CeO_4, was identified by a combinatorial materials synthesis technique. This material was further synthesized using the chemical coprecipitation method and the decomposition of acetates, carbonates and oxalates in a tedious procedure. In this work, we present the use of Pechini's method as an alternative for the synthesis of this promising material. When the precursor, (Sr/Ce) polymer citrate–ethylene glycol, was fired at 850°C for 2 h, a mixture of Sr_2CeO_4 and $SrCeO_3$ (inactive) was obtained, whereas the amount of Sr_2CeO_4 was increased by further heating at 1100°C for 2 h in an oxygen atmosphere, as shown by the diffraction pattern. The excitation spectra present two broad bands with maxima at 294 and 344 nm and the emission spectrum has a broad band (half width ~80 nm) centered at ~475 nm. The unusually long lifetime of the compound fired at 1100°C of ~0.04 ms is in good agreement with literature data. In conclusion, the blue phosphor material Sr_2CeO_4 synthesized at 1100°C in an oxygen flux has comparable or even better emitter properties than that prepared over several days and/or at higher temperatures. The method is very attractive for industrial purposes.

Keywords: Phosphors; Chemical synthesis; X-ray diffraction; Optical properties; Luminescence

1. Introduction

Lanthanide ions offer almost unlimited possibilities for the design of new luminescent materials. When excited, these materials convert energy into electromagnetic radiation in the visible and/or infrared. Energy absorption is through the matrix and/or a sensitizer and the final emission by the lanthanide ion [1–4]. The search for phosphors started more than 100 years ago and applications have regularly been developed, mainly in photonic and electro-luminescent devices. The luminescence of rare earth based phosphors also permits the development of trichromatic luminescent lighting, the white color being produced by the emission in the blue, green and red, respectively, at 450, 550 and 610 nm. The green and red are produced by the f–f transitions of Tb^{3+} and Eu^{3+}, while the blue emission is produced by the f–d transition of Eu^{2+}. Very satisfactory red and green commercial phosphors are being produced, but comparable materials for the blue emission are still lacking [4–7], and are under development for practical applications [8,9].

Recently, a blue phosphor, Sr_2CeO_4, was identified by combinatorial chemistry [10] and prepared by the decomposition of carbonates, acetates and oxalates [11,12]. The described methods always use temperatures above 1000°C for periods as long as 48 h. Due to success in the preparation of Eu^{3+} oxides and oxosalt phosphors [13] we used the method of Pechini in order to obtain Sr_2CeO_4 [14]. This method is primarily used to obtain oxide electrodes and begins with polybasic chelates which are formed between hydroxycarboxylic acids (e.g. citric acid) and metallic ions. The chelate undergoes polyesterification upon heating with a polyfunctional alcohol (e.g. ethylene glycol) to form a resin intermediate. Combustion of this resin at low temperature removes the organic material and yields the selected composition of doped oxides or oxosalts. Among the advantages of this method are the possibility of preparing complex compositions, obtaining good homogeneity through mixing at the molecular level in solution and stoichiometric control [14]. Luminescent and X-ray spectroscopy were used to characterize the materials.

2. Experimental

Strontium and cerium citrates were prepared from appropriate mixtures of nitrates (Sr^{+2}/Ce^{+3}, 2:1) with

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citric acid and ethylene glycol in aqueous media. The solution was carefully heated until ~120°C, leading to a yellowish polymeric resin that was fired at 850 or 1100°C under ambient or oxygen atmosphere for 2–4 h.

Excitation and emission spectra were recorded at room temperature with a Fluorolog 3 Jobin-Yvon/SPEX spectrofluorometer from ISA. Luminescent decay curves were measured under pulsed Xe lamp excitation using the phosphorimeter accessory 1934D. X-ray powder diffraction data (XRD) were collected using a D 5005 X-ray diffractometer from Siemens. Search and matching for Sr and Ce compounds was carried out using the EVA program.

3. Results and discussion

The excitation spectra, $\lambda_{em} = 475$ nm (Fig. 1), for the four samples are quite different. The samples heated at 850 and 1100°C in the absence of oxygen presented maxima at 275/356 and 294/344 nm, respectively, while in the presence of oxygen the maxima were at 285/355 and 293/345, respectively. At higher temperatures the bands at ~280 nm decrease, while the bands at ~350 nm increase. The presence of oxygen increases both maxima. The emission spectra for all samples are very similar (Fig. 2) with maxima at 470–480 nm depending on the firing temperature and the presence of oxygen. For the sample fired at 1100°C both maxima show similar spectra. The CIE chromaticity index is $x = 0.16$ and $y = 0.21$, which is better [5] than that reported by Danielson ($x = 0.20$ and $y = 0.30$) [10] and Jiang ($x = 0.19$ and $y = 0.26$) [12]. The spectral properties of these compounds are attributed to ligand (O^{2-}) to Ce $^{4+}$ charge transfer [10], resulting in broad bands and long lifetimes (40 and 44 μs for the compounds fired at 850 and 1100°C, respectively). The lifetimes for the Ce^{3+} (5d–4f) emissions are on the scale of nanoseconds.

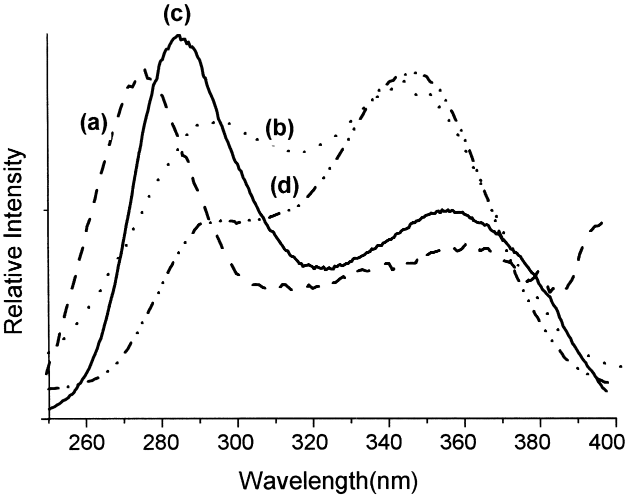

Fig. 1. Excitation spectra ($\lambda_{em} = 475$ nm) of the samples heated at (a) 850°C and (b) 1100°C in air and (c) 850°C and (d) 1100°C in an oxygen flux.

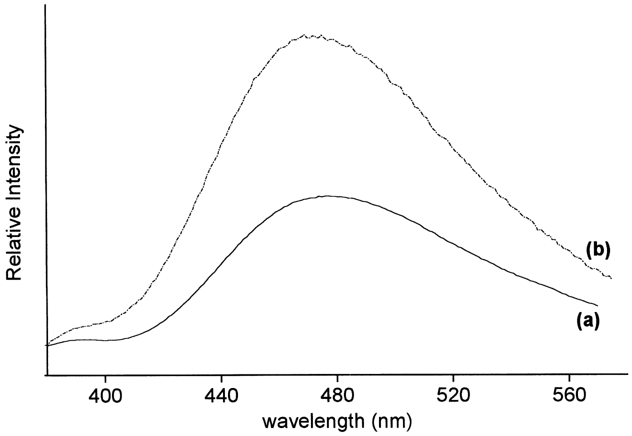

Fig. 2. Emission spectra ($\lambda_{ex} = 345$ nm) of the samples heated at (a) 850°C ($\lambda_{ex} = 275$ nm) in air and (b) 1100°C ($\lambda_{ex} = 294$ nm) in an oxygen flux.

For the compound fired at 1100°C the XRD pattern is consistent with the triclinic structure of Sr_2CeO_4 presented on the JCPDS card (2214-22) as pointed out by Jiang [12]. The XRD patterns present some additional cerianite (CeO_2) (JCPDS 43-1002) but no $SrCeO_3$ (JCPDS 23-1412), even in the materials fired at lower temperatures and/or in the absence of a pure oxygen flux. Pechini's method proved to be very promising for the controlled preparation of this blue phosphor material, with an even better CIE chromaticity index than reported previously.

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References

[1] T. Justel, H. Nikol, C.R. Ronda, Angew. Chem. Int. Ed. 37 (1998) 3084.
[2] K.D. Oskan, R.T. Wegh, H. Donker, E.V.D. Loef, A. Meijerink, J. Alloys Comp. 300 (2000) 421.
[3] P. Benalloul, C. Barthou, J. Benoit, J. Alloys Comp. 275 (1998) 709.
[4] A.C. Vaz de Araujo, I.T. Weber, B.S. Santos, B.J.P. Silva, R.P. Mello Jr., S. Alves Jr., G.F. de Sa, C.M. Donega, J. Non-Cryst. Solids 219 (1997) 160.
[5] C.R. Ronda, J. Alloys Comp. 225 (1995) 534.
[6] P. Maestro, in: R. Saez, P.E. Caro (Eds.), Rare Earths, Editorial Complutense, Madrid, 1998, p. 317.
[7] T.X. Sun, Biotechnol. Bioeng. 61 (1999) 193.
[8] M. Dejneka, E. Snitzer, R.E. Riman, J. Lumin. 65 (1995) 227.

[9] H. Yamamoto, M. Mikami, Y. Shimomura, Y. Oguri, J. Lumin. 87 (2000) 1079.
[10] E. Danielson et al., Science 279 (1998) 837.
[11] E. Danielson et al., J. Mol. Struct. 47 (1998) 229.
[12] Y.D. Jiang et al., Appl. Phys. Lett. 74 (1999) 1677.
[13] O.A. Serra, S.A. Cicillini, R.R. Ishiki, J. Alloys Comp. 303 (2000) 316.
[14] M.P. Pechini, US Pat. 3 330 697, 1967.