



Influence of vinyltriethoxysilane concentration on structural and luminescent characteristics of cerium doped yttrium based silicate phosphors

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Abstract

Cerium doped yttrium silicates phosphors (YSO:Ce) were prepared by gel combustion using vinyltriethoxysilane (VTEOS) as silicon sources along with aspartic acid as fuel and yttrium-cerium nitrate as oxidizer. The study presents the influence of VTEOS amount in the synthesis mixture on the structural and luminescent characteristics of silicate phosphors. The understanding of precursor's decomposition was achieved on the basis of thermal analysis in association with gas evolved analysis. XRD, FTIR and XPS were used to reveal the structural changes that occur with VTEOS molar amount variation from 1 to 3 mol. It was found that the main crystalline phase was X2-Y₂SiO₅. The luminescent characteristics of phosphors were measured at room and low temperature (10–300 K) based on emission and excitation spectra. Under UV excitation, YSO:Ce exhibits blue emission due to electron transition in Ce³⁺ from 5d level to the ground state levels (²F_{5/2}, ²F_{7/2}). The emission intensity increases from 70% to 120% along with VTEOS amount, explained by the improvements in structural homogeneity. Incorporation of cerium in different sites (Ce1 and Ce2) is discussed based on PL and PLE spectra measured at low temperature (10 K).

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1. Introduction

Yttrium mono-silicate (Y₂SiO₅) and di-silicate (Y₂Si₂O₇) have been widely investigated in the recent decades due to their high chemical and thermal stability. If doped with different metallic ions, these materials exhibit attractive luminescent properties for potential applications such as: plasma displays [1], laser materials [2] and high-energy phosphors [3]. Y₂SiO₅ possesses two different crystallographic forms (X1 and X2) while Y₂Si₂O₇ shows up to six polymorphic forms (γ, α, β, γ, δ, z). All of them are stable in a certain temperature range [4,5]. It is interesting to reveal that a particular phase may be associated with the specific preparative conditions, for instance, sol–gel techniques favors formation of α-Y₂Si₂O₇ phase and hydrothermal synthesis assures

formation of γ-Y₂Si₂O₇ phase [6–8]. Studies regarding the structural changes in Y₂SiO₅ and Y₂Si₂O₇ have been performed for temperatures between 900 °C and 1400 °C. It was found that, X1-Y₂SiO₅ phase is transformed into X2 phase at around 1190 °C [9,10]. On the other hand, α-Y₂Si₂O₇ phase begins to crystallize at ~1000 °C and totally converts into β form at 1400 °C [11,12].

According with the phase diagram, a molar composition of 50% mole Y₂O₃ and 50% mole SiO₂ leads to yttrium mono-silicate formation. If the amount of SiO₂ increases up to 67% mole, yttrium mono- and di-silicates are identified, while over 67% mole, unreacted SiO₂ along with di-silicate are observed [13].

The preparation of rare earth mono- or di-silicate phosphors was performed using solid state, sol gel, hydrothermal, coprecipitation and spray pyrolysis methods [14–17]. It was given a great attention to the study that shows the role of different preparative conditions (concentration and type of activators, firing temperature etc.) on the phosphor's characteristics

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[11,18]. Improvements on the luminescent characteristics and morphology of silicate phosphors can be done using mineralizing agents like: NaCl, BaF₂, H₃BO₃ or Li₂SO₄ [18,19,20].

Based on the literature survey we found that silica (SiO₂) and tetraethoxysilane (TEOS) are the most used silicon providers in solid state reactions, combustion [21,22] and sol gel techniques [23]. For example colloidal SiO₂ obtained from hydrolysis of TEOS can be used in reaction with nanostructured Y₂O₃:Ln³⁺ in order to prepare nanocrystalline Y₂Si₂O₇ [24].

Very few studies are focused on finding new silicon sources in order to highlight their effect on the morphostructural and luminescent characteristics of silicates based phosphors. Lei et al, showed that N-2-aminoethyl-3-aminopropyltrimethoxysilane chosen among other seven types of silicon sources, gives the best results regarding the luminescent behavior of silicates [25]. Recently, silicon resins (polysiloxanes) in different solvents (i.e. isopropyl alcohol) mixed with nano-sized powders of Y₂O₃ were used for preparation of mono and yttrium disilicate [26].

The increasing demand for high performance phosphors requires either finding new synthesis methods or optimizing the preparative conditions of the existing ones. In this direction, the search of new silicon sources becomes an issue of great importance. Our previous work showed that combustion of TEOS in association with aspartic acid led to the synthesis of single phase silicate phosphors with intensive luminescence [27]. In this paper we used vinyltriethoxysilane (VTEOS) as a new silicon source in various amounts to emphasize its effect on the structural changes and the implications on luminescent characteristics of silicate phosphors. We found that the use of VTEOS as silicon source compared with TEOS [27] led to samples with 25% higher luminescence.

2. Experimental part

2.1. Materials

The preparation of cerium doped yttrium silicate phosphors by gel-combustion was done using the following starting materials: yttrium oxide (99.9%, Alfa Aesar), cerium nitrate hexahydrate as rare earth ions sources (extra pure, Merck), L-aspartic acid as fuel (99.0%, Alfa Aesar), vinyltriethoxysilane as silicon source (97% Alfa Aesar). Ethanol (94–96% Alfa Aesar) was added during the gelation process.

2.2. Sample preparation

A detailed description of synthesis was presented in our previous work [27]. Briefly, the synthesis takes place in three steps namely: (1) *preparation of gels* at 80 °C from a solution containing yttrium-cerium nitrates, aspartic acid and VTEOS; (2) *formation of ashes* by the combustion of gels at 350 °C and (3) *preparation of the phosphors* by thermal treatment of the ashes at 1400 °C for 4 h in air atmosphere. Several samples containing 1.5% mole Ce/mole Y+Ce were prepared using various amounts of VTEOS that are systematized in Table 1.

Table 1
Samples prepared with different amounts of VTEOS.

Y(NO ₃) ₃ +Ce(NO ₃) ₃ (Mole)	VTEOS (Mole)	Molar ratio Si/ Y+Ce	Sample code
2.00	1.00	0.50	^a VTEOS ₁
2.00	1.25	0.63	VTEOS _{1,25}
2.00	1.50	0.75	VTEOS _{1,5}
2.00	2.00	1.00	^b VTEOS ₂
2.00	3.00	1.50	VTEOS ₃

^aStoichiometric for Y₂SiO₅.

^bStoichiometric for Y₂Si₂O₇.

In order to designate the status of the samples during the synthesis stages we used the following terms: ‘gel’ (samples obtained after gelling); ‘ash’ (samples prepared after combustion) and ‘phosphor’ (samples after thermal treatment).

To compare the emission intensity from above prepared phosphors, a single phase X2-Y₂SiO₅:Ce sample was prepared by solid-state reaction. In this respect proper amounts of Y₂O₃ (Aldrich), Ce(NO₃)₃ (Aldrich) and SiO₂ (fumed- Aldrich) were mixed and homogenized with water, dried at 115 °C and finally fired at 1400 °C for 4 h in air atmosphere. This sample is considered to have the luminescent emission of 100% and is taken as internal standard.

2.3. Sample characterization

Precursors were investigated by thermogravimetric and differential thermal analysis with a Mettler Toledo TGA/SDTA851 instrument in a platinum crucible, with the heating rate of 20 °C/min under nitrogen flow of 30 mL/min. Correlations between the thermal decomposition steps, mass loss, and composition of gases evolved during the thermal treatment, were established using TG-DTA-FT-IR coupled system. Evolved gas analysis (EGA) was done with a Thermo Scientific Nicolet 6700 FT-IR Spectrometer equipped with TGA module, working at 210 °C. The composition of the evolved gases has been identified using the FT-IR spectra library i.e. HR Nicolet TGA Vapor Phase. FT-IR analysis of the ashes and gels was recorded by using a JASCO 610 Spectrometer (KBr pellets technique).

The structural and luminescent characteristics of yttrium silicate phosphors were investigated using the usual methods for materials characterization. In this respect, the crystalline structure was determined by X-ray diffraction (XRD), a 6000 Shimadzu diffractometer at voltage 40 KV and 30 mA using Cu Kα1 radiation (1.54056 Å) in the 2θ range 10–80°. The qualitative compositions of samples were investigated by X-ray Photoelectron Spectroscopy (XPS) using a SPECS spectrometer working with Al anode (1486.6 eV) and assisted by Ar ions etching. Each sample was subjected to several Ar ion etchings until the XPS spectra remained unchanged in shape and intensity.

Surface area measurements were performed with a Micromeritics TriStar II 3020 instrument, nitrogen adsorption at 77 K. All samples were degassed at 150 °C for 24 h in nitrogen

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