NOVEL METHOD FOR THE SYNTHESIS OF Dy-DOPED YTTRIUM DISILICATE PHOSPHOROS

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Abstract

The complex high temperature polymorphism (Y, α, β, γ and δ structures) of yttrium disilicate ($Y_2Si_2O_7$) naturally lead to relatively broad emission, originating from ions placed in different symmetry sites, for example, the replacing of Y^{3+} by rare earth ions. $Y_2Si_2O_7$ as the host lattice shows a high thermal and chemical stability compared with other well-studied phosphors such as ZnS and CdS. When doped with different metallic ions, yttrium silicates exhibit attractive luminescent properties for potential applications, such as plasma displays, laser materials and high-energy phosphors. The sol-gel technique provides an available method to prepare ceramic powders, with higher purity and homogeneity compared to the conventional solid-state reaction of mixed oxides. In the present work, a novel sol-gel and co-precipitation combined method has been proposed for synthesis of RE^{3+} doped $Y_2Si_2O_7$ (RE=Dy). Silica nanoparticles were obtained by surfactant-assisted sol-gel process, using sodium silicate (Na_2SiO_3) as precursor, and then Y^{3+} and Dy^{3+} ions were precipitated over these particles. The RE^{3+}:$Y_2Si_2O_7$ obtained product was analyzed by SEM, XRD and luminescence spectroscopy. Crystalline $Y_2Si_2O_7$ was obtained at lower temperatures compared with traditional methods. The α-phase was obtained at 1100 and 1200°C, and β-phase at 1300°C. Comparing photoluminescence spectra of α and β-phases, the later showed higher intensity luminescence peaks.

Keywords: yttrium disilicate, phosphors, sol gel, coprecipitation, luminescence

Introduction

Yttrium disilicate/pyrosilicate ($Y_2Si_2O_7$), which occurs naturally as yttrialite, is a mixture of rare earth silicates. It displays interesting structural properties because of its high refractoriness (mp = 1775 °C) and stability in oxidizing environments. $Y_2Si_2O_7$ is also found in grain boundaries of Si_3N_4, when yttria (Y_2O_3) is used as sintering aid, and its presence has been reported to improve the high temperature mechanical properties of silicon nitride [1,2]. It should be pointed out that yttrium disilicate, with its wide band gap and excellent thermal and chemical stability, as compared with other well-studied phosphors such as ZnS and CdS, has been shown to be one of the most efficient host lattices for rare earth ions, which substitute Y^{3+} ions [3-5]. When doped with different metallic ions, yttrium silicates exhibit attractive luminescent properties for potencial applications, such as plasma displays, laser materials and high-energy phosphors [6]. $Y_2Si_2O_7$ presents five polymorphs (Y, α, β, γ, δ) that have been studied and revised in the past by several authors. One of them, the yttriallite low form, also called y, is only stable up to 1200ºC and can contain "stabilizing impurities" [7] such as H^+, Na^+, Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Th^{4+} or Zr^{4+}. Different polymorph structures naturally lead to relatively broad emission originating from ions placed in different symmetry sites, which is the reason why there are few detailed works reported for $Y_2Si_2O_7$ doped with RE^{3+} ions [4]. However, some controversy remains with regard to the stability of the different polymorphs. In particular, it has been pointed out that the crystallization mechanism is strongly related to the synthesis route employed and the thermal history. The synthesis methods commonly used to prepare yttrium disilicate are the conventional solid-state reaction of mixed oxides Y_2O_3 and SiO_2, and the calcination of yttrium disilicate precursors synthesized by sol-gel and hydrothermal processing [1]. It is interesting to reveal that a particular phase may be associated with the specific preparative conditions, for instance, sol–gel techniques favors the formation of α-$Y_2Si_2O_7$ phase and hydrothermal synthesis assures formation of y-$Y_2Si_2O_7$ phase [6]. In the present work, Dy-doped yttrium silicate was prepared by combination of sol-gel and coprecipitation methods. Silica particles were obtained by surfactant-assisted sol-gel process, using sodium silicate (Na_2SiO_3) as precursor, and then Y^{3+} and Dy^{3+} ions were precipitated over these particles. The obtained product was observed by SEM, XRD and luminescence spectroscopy .

Materials and methods

The following reagents were used as starting materials: sodium silicate solution (Na_2SiO_3), with silica concentration of 64,64 $g.L^{-1}$, hydrochloric acid (HCl) 12M (Merck), fatty amine surfactant Ethomeen HT/60 (AkzoNobel), hexahydrated yttrium nitrate solution ($Y(NO_3)_3 . 6 H_2O$), solid dysprosium nitrate ($Dy(NO_3)_3 . 6 H_2O$), and sodium hydroxide (NaOH) as precipitating agent. Previously, the surfactant was diluted in ethanol and hydrochloric acid to obtain a solution with 83 $g.L^{-1}$ concentration. To synthetize silica particles, 18 ml of hydrocloric acid, 1.6 ml of surfactant solution and 8.6 ml of sodium silicate were stirred in a beaker, and the solution was kept in rest for 24 h to form the gel of silica. Subsequently, 0,215 g of dysprosium content in nitrate solution were added to the gel under magnetic stirring. Then NaOH was added dropwise to the mixture (gel + Dy nitrate), to precipitate a white Dy hydroxide. The resulted product was filtered and washed with water to remove impurity ions, and later calcined to different temperatures to obtain Dy-doped crystalline yttrium disilicate powder. Four samples were produced, and labeled YD-11, YD-12, YD-13 and YD-14, which were calcined at 1100, 1200, 1300 and 1400ºC for 1 h, respectively. The powders were characterized with XRD analyses using Cu-Kα radiation (λ: 1.54 Å) in Rigaku DMAX 2000 diffratometer.

Results and discussion

Figure 1 shows the XRD patterns of the samples of $Y_2Si_2O_7:Dy^{3+}$.

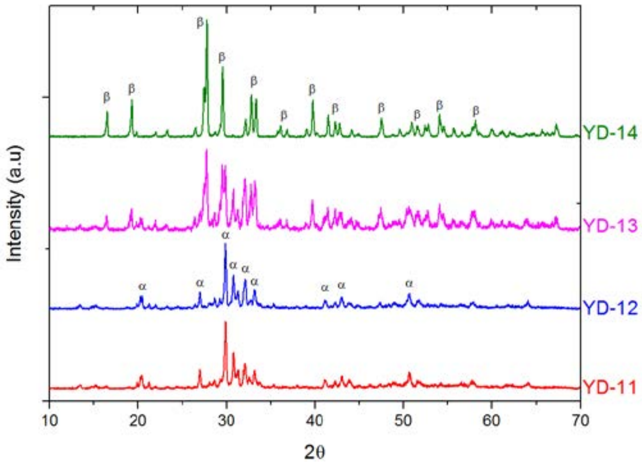

Figure 1- XRD patterns of $Y_2Si_2O_7:Dy^{3+}$samples calcined at different temperatures.

The XRD pattern of the samples YD-11 and YD-12 (calcined at 1100 and 1200°C, respectively) were identified as the α-$Y_2Si_2O_7$ (PDF 21-1457), while the samples calcined at 1300 and 1400°C were identified as β-$Y_2Si_2O_7$ (PDF 21-1454 and 22-1103). This transition temperature between α and β-phases is according to that of the temperature range established by Ito and Johnson [9].

Fig. 2 shows SEM images of the Dy-doped yttrium disilicate samples. The images were obtained from a Tabletop TM-3000 microscope.

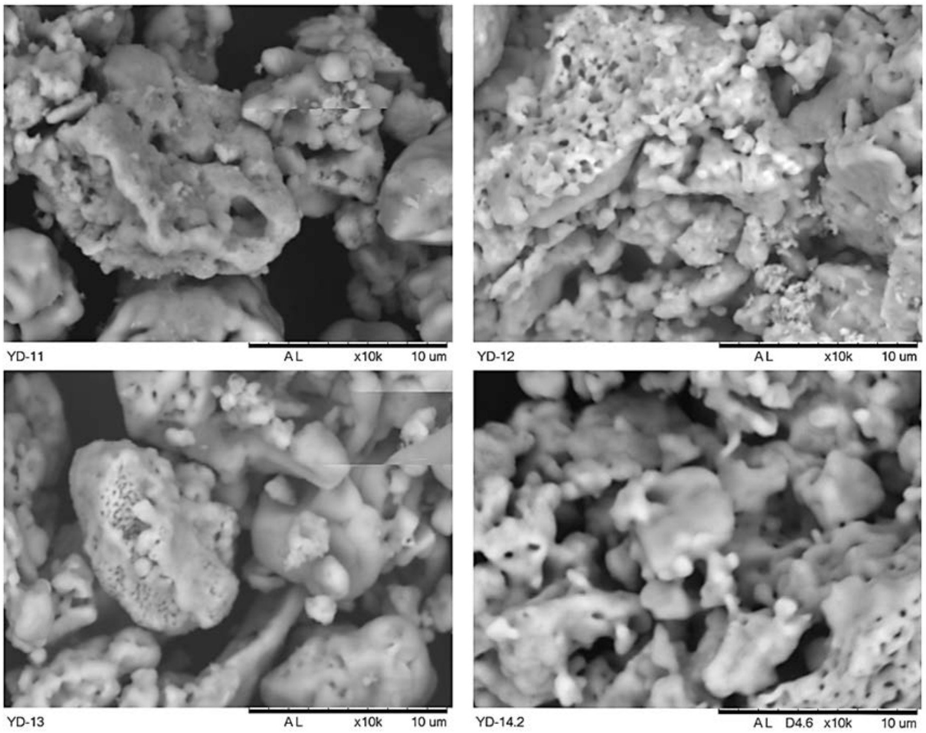

Fig. 2. SEM images of $Y_2Si_2O_7$:Dy^{3+}samples

In the above images it is possible to observe porous agglomerates, and the coalescence between particles, which shows the powder sintering. It is also possible to observe the presence of some spherical particles.

Figures 3 and 4 shows emission and excitation spectra of α-phase (samples YD-11 and YD-12) and β-phase of yttrium disilicate (YD-13 and YD-14), respectively. The spectra were obtained from a Fluorolog 3 fluorimeter (Jobin Yvon),

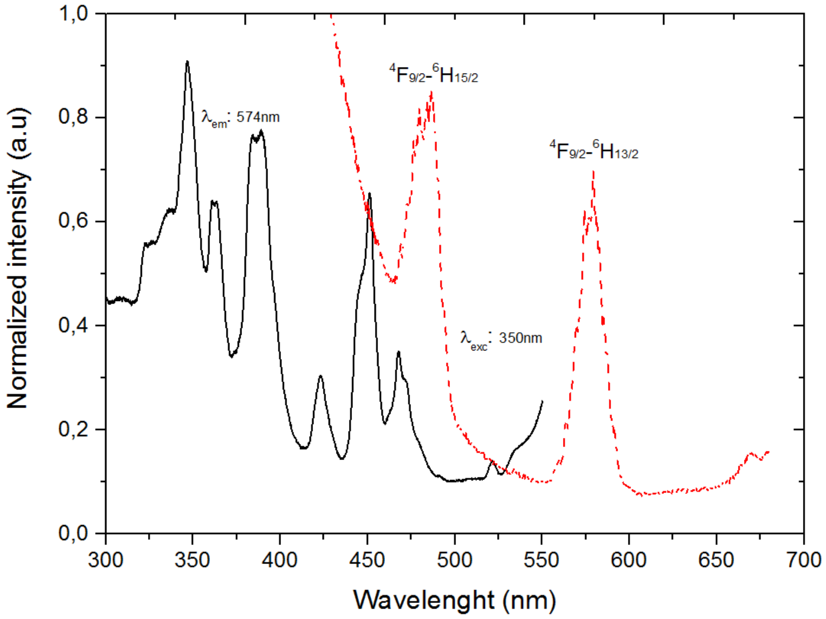

Fig. 3. Room-temperature emission (dashed line) and excitation (solid line) spectra for the α-phase of $Y_2Si_2O_7:Dy^{3+}$ (samples YD-11 and YD-12)

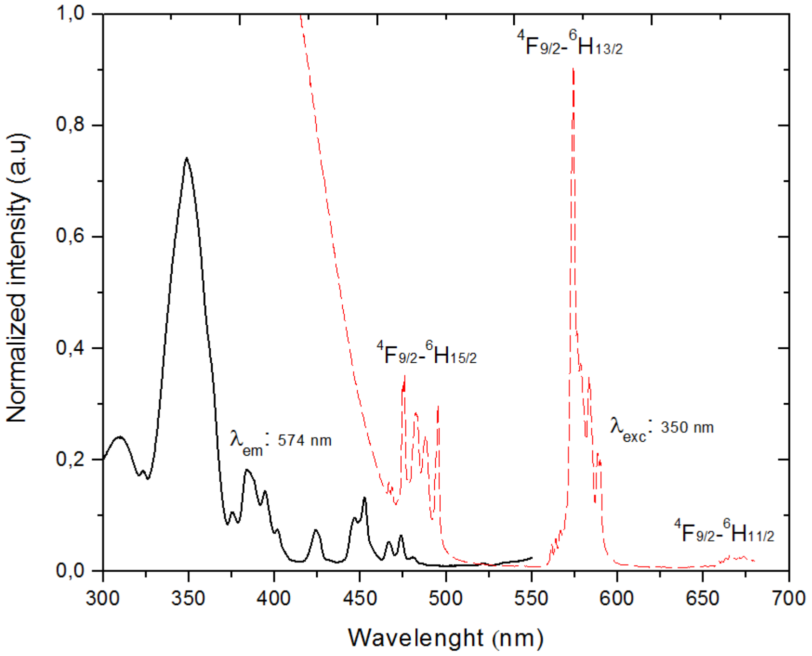

Fig. 4. Room-temperature emission (dashed line) and excitation (solid line) spectra for the β-phase of $Y_2Si_2O_7:Dy^{3+}$ (samples YD-13 and YD-14)

The excitation spectra peaks correspond to the transition of the Dy^{3+} ground state $^6H_{13/2}$ to the excited states $^6P_{7/2}$ (348 nm), $^6P_{5/2}$ (362 nm),$^4I_{13/2}$ (387nm), $^4G_{11/2}$ (423 nm), $^4H_{11/2}$ (452 nm) and $^4F_{9/2}$,(470 nm) [10]. The emission spectra peaks correspond to the transitions $^4F_{9/2}$-$^6H_{15/2}$ (~480 nm – blue region), $^4F_{9/2}$-$^6H_{13/2}$ (~575 nm – yellow region), $^4F_{9/2}$-$^6H_{11/2}$ (~670 nm – red region) [10,11]. It is possible to observe that, the transitions $^4F_{9/2}$-$^6H_{15/2}$ and $^4F_{9/2}$-$^6H_{13/2}$ show similar intensities (with $^4F_{9/2}$-$^6H_{15/2}$ showing a slightly bigger intensity), in α-phase. The transition $^4F_{9/2}$-$^6H_{13/2}$ dominate over $^4F_{9/2}$-$^6H_{15/2,}$ in β-phase (both of which show sharper peaks than in α-phase) and it also displays the transition $^4F_{9/2}$-$^6H_{11/2,}$ although with very low intensity. Diaz et al [8] previously reported the high luminescence efficiency of β-phase.

Conclusions

In this work, pure, single-phase, dysprosium-doped yttrium disilicate phosphors was synthesized via combination of sol-gel and co-precipitation methods. Due to greater homogeneity and easy stoichiometry control of the applied method, crystalline yttrium disilicate was obtained at lower temperatures than compared with traditional way. The α-phase was reached at 1100 and 1200°C, and β-phase starting to form at 1300°C. Comparing photoluminescence spectra of α and β-phases, the β-phase showed higher intensity luminescence peaks.

Acknowledgments

This work was supported by FAPESP, São Paulo Research Fundation.

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