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Concentration and Cyrstalline Phase Effects on the Spectroscopic Properties of Sol-Gel Synthesized Er^{3+}:$Y_2Si_2O_7$ Nanopowders

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Abstract: Nanosized yttrium disilicate powders activated with trivalent erbium ions were produced by Sol-Gel known as wet chemical process. The structure and morphology of the synthesized powders were characterized by using X-ray diffraction spectroscopy (XRD), Transmission electron microscopy (TEM) and Photoluminescence spectroscopy. The XRD analysis revealed that the formation of triclinic α-$Y_2Si_2O_7$ and monoclinic β-$Y_2Si_2O_7$ polymorphs were obtained at 1050 °C and 1450 °C, respectively. The photoluminescence properties were also investigated in terms of sintering temperature and doping effect on different polymorphs.

Sol-Jel ile Sentezlenmis Er^{3+}:$Y_2Si_2O_7$ Nanofosforların Spektroskopik Özellikleri Üzerinde Konsantrasyon ve Faz Etkileri

Anahtar Kelimeler
Itriyum disilikat,
Nanofosfor,
Faz özellikleri,
Sol-Jel

Özet: Üç elektron değerlikli erbiyum iyonları ile katkılandırılmış nanoboyutlu Itriyum Silikat tozları yaş kimyasal bir yöntem olarak bilinen Sol-Jel ile üretilmişlerdir. Sentezlenen tozlar X-Işınları spektroskopisi (XRD), geçişli elektron mikroskopisi ve fotolüminesans spektroskopisi yöntemleri kullanılarak karakterize edilmişlerdir. XRD analizi sonuçlarında, 1050 °C ve 1450 °C de sentezlenen tozlar sırasıyla triklinik α-$Y_2Si_2O_7$ ve monoklinik β-$Y_2Si_2O_7$ kristal poliform yapılarını göstermiştir. Tavlama sıcaklığı ve farklı poliform yapılar üzerindeki katkılamanın etkisi bakımından fotolüminesans özellikleri ayrıca araştırılmıştır.

1. Introduction

Yttrium silicates (Y_2SiO_5 and $Y_2Si_2O_7$) are promising materials due to the electrical, magnetic and optical properties in the fields of photonics [1-5]. They are also ideal candidates for environmental barrier coating (EBC) and dental applications due to their excellent high temperature properties [6-10].

Yttrium disilicate ($Y_2Si_2O_7$) is one of the binary disilicates with high thermal and chemical stability (Melting point : 1775 °C), low dielectric constant, low linear coefficient of thermal expansion and low thermal conductivity. It shows y, α, β, γ, and δ phases because of complex polymorphism resulting in comparative broad emission [11-12]. It is very difficult to obtain a pure phase of yttrium disilicate because of its intricate polymorphous structure.

Rare earth elements (RE) doped, co-doped and tri-doped $Y_2Si_2O_7$ are crucial nanophosphors for lasers, light emitting diodes (LED), white LED and plasma display panel applications [13-16]. Although, various rare earth-activated yttrium orthosilicates have been studied a lot [17-28], there have been a few studies reported on the Er^{3+} : $Y_2Si_2O_7$. Diaz et al. analyzed the luminescence properties of $Y_2Si_2O_7$: Dy phosphors prepared by a new pressureless hydrothermal route. Their results indicated that the efficiency of Dy-doped β-$Y_2Si_2O_7$ phase is approximately 40% of that measured for the commercial phosphor Eu-Y_2O_3 [17]. Hreniak et al. studied the spectral output of $Y_2Si_2O_7$: Tb, $Y_2Si_2O_7$: Er, Yb and $Y_2Si_2O_7$: Pr, Yb glass, thin film and phosphor materials synthesized by the sol–gel method. They have found that the luminescence properties and lifetimes depend strongly on annealing temperature [18-19]. Zhou et al. synthesized the nanocrystalline $Y_2Si_2O_7$: Eu phosphors with an average size of 60 nm using silica

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aerogel as raw material. Compared with Y_2O_3/SiO_2 crystalline, they declared that the excitation and emission peaks of nanocystalline red-shifted and leaded to enhance of its luminescence intensity [20]. Li et al. synthesized $Y_2Si_2O_7$: Eu, $Y_2Si_2O_7$: Tb and $Y_2Si_2O_7$: Ce,Tb phosphors via sol-gel method. They focused on energy transfer mechanisms between Tb^{3+} and Ce^{3+} ions and discussed photoluminescence intensity on Re^{3+} concentration in detail [21-22]. Thanh et al. studied the structure of $Y_2Si_2O_7$: Ce phosphors prepared by the sol-gel method with added ammonia. The blue light was emitted when excited by the 325 nm UV radiation[23].

Sokolnicki investigated the upconversion luminescence from Er^{3+} in nanocrystalline $Y_2Si_2O_7$: Er and $Y_2Si_2O_7$: Yb, Er and produced $Y_2Si_2O_7$: Ce, Eu, Tb phosphors by combustion and sol-gel techniques. The white light emission is obtained by varying the concentration of the active ions and treating atmosphere [14, 24]. Marciniak et al. presented the spectroscopic properties of $Y_2Si_2O_7$: Er^{3+} nanocrystalline powder and thin film synthesized by the sol-gel method [25].

In our former studies, we have discussed the structural and spectroscopic properties of $Y_2Si_2O_7$: Nd and $Y_2Si_2O_7$: Yb phosphors [26, 27] and the up-conversion properties of $Y_2Si_2O_7$: Yb, Er nanophosphors obtained by sol-gel technique [28].

In the present study structural characterization and the spectroscopic properties of Er^{3+} doped nanocrystalline yttrium disilicate samples fabricated using sol-gel method are reported depend upon cyrstalline phase properties. Due to the efficient luminescence properties at the telecommunication wavelength of 1.54 μm, Erbium doped materials have received considerable interest in optical amplifiers and silicon photonics [15, 29].

2. Material and Method

Er^{3+} : $Y_2Si_2O_7$ nanopowders were synthesized in the phase diagram of SiO_2-Y_2O_3 binary system using the sol–gel method to obtain two different phases. TEOS (Si $(OC_2H_5)_4$) with 99.9% purity, yttrium nitrate (Y (NO_3) $\cdot 6H_2O$), and erbium nitrate (Er (NO_3) $\cdot 5H_2O$) salts with 99.9% purity were used to produce the nanopowders. Detail explanation of the fabrication process could be reached in our recent study [28]. The fabricated samples were then annealed at 1050 °C and 1450 °C for 12 hours to produce nanocrystalline $Y_2Si_2O_7$ powders. Three different samples were synthesized with 0.5, 1.0, 1.5 mol % ratios for Er^{3+} ions; they were labeled as YSE1, YSE2, YSE3, respectively.

The structural properties of two powders were conducted using X-ray diffraction spectroscopy (Model of Rigaku–XRD 2200 D/MAX) with the Cu-Kα source operated with the wavelength at $\lambda = 1.5418$ Å. Slit systems, step-size (0.02°), source voltage (40 kV), and current (30 mA) were kept constant during the scans that were conducted in θ–2θ coupled mode. The morphological properties of the powders were also investigated by TEM with model number JEOL JEM-2100.

The photoluminescence (PL) spectrums of all powders were conducted using a diode laser (Laser Drive Inc.-LDI-820) with a wavelength of 800 nm. The emissions resulting from the dopant ions of the powders were transmitted to a Monochromotor (McPherson Inc. Model 2051) and measured by an InGaAs semiconductor detector (Princeton Inc. Model ID-441-C) with a preamplifier (Stanford Res. Model SR560). A short wavelength pass filter (800 nm) was placed infront of the monochromator to eliminate the scattering lights in the measurements.

The decay measurements of the dopant ions in the powders under pulsed excitation were taken by using the titanium sapphire laser (Model of Schwarz Electro–Optics Inc. Titan–P) and a digital oscilloscope (Model of Tektronix- TDS3052B). All spectral output of the nanopowders was recorded at room temperature.

3. Results and Discussion

3.1. X-ray diffraction analysis

The phase evolution of the phosphors heat-treated at different temperatures was determined using X-ray diffraction analysis. The XRD patterns of the Er^{3+} doped $Y_2Si_2O_7$ (YSE1, YSE2 and YSE3) samples calcined at two different temperatures are shown in Figure 1.

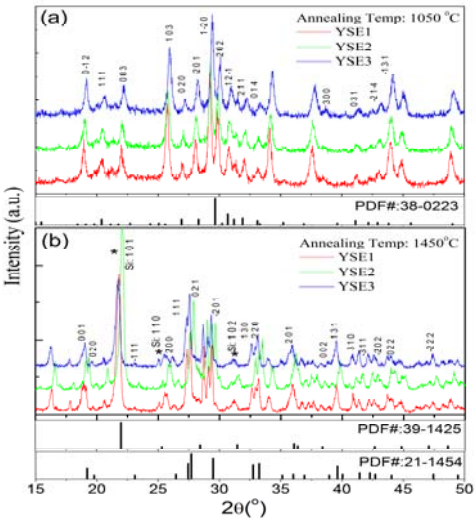

Figure 1. The X-ray patterns of YSE powders calcined at **(a)** 1050 °C, **(b)** 1450 °C.

It can be seen in Figure 1a, 1b that α-$Y_2Si_2O_7$ (JCPDS file no. 38-0223) is the dominant (main) phase for the Er^{3+} doped powders calcined at 1050 °C. Annealing the samples to 1450 °C resulted in the growth of the

β-$Y_2Si_2O_7$ crystalline phase which is well consistent with the JCPDS file no. 21-1454. We observed also the presence of the SiO_2 (JCPDS file no. 39-1425) peak located at $2\theta = 22°$ (indicated with an asterix $*$ in Figure 1b). Similar results have been recently reported by Becerro et al and Diaz et al. [30, 31]. The structure of the other phases and the intensity of the peaks do not change as a function of Er^{3+} doping concentration, indicating that the doping ions do not contribute to the formation of new phases.

The polymorphs of yttrium disilicates transform from one phase into another with increasing temperature [32]. However, phase transition temperatures vary considerably in the studies of different researchers [17, 18, 33, 34]. This demonstrates that the yttrium disilicate structure is strongly dependent on the synthesis methods, annealing temperatures and pressure.

3.2. Transmission electron microscopy results

Morphological properties and the particle size distribution of calcined powders were identified with transmission electron microscope. Figure 2 illustrates the TEM images of 1.0% Er^{3+} doped yttrium disilicate samples (YSE2) annealed at 1050 °C and 1450°C. The yttrium disilicate powders have regular crystalline form and the particle size of crystallites increase with the increasing annealing temperatures. The average size of nano particles estimated from TEM images is about ~100 nm for α-$Y_2Si_2O_7$, and 0.5 μm for β-$Y_2Si_2O_7$.

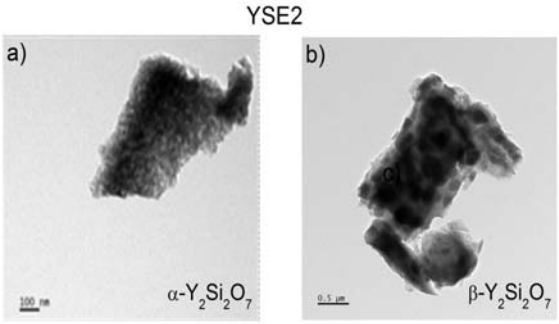

Figure 2. The TEM images of 1.0% Er^{3+} doped yttrium disilicate samples (YSE2) annealed at **(a)** 1050 °C, **(b)** 1450 °C.

3.3. Photoluminescence (PL) properties

Figure 3 shows the spectral output of photoluminescence measurement of Er^{3+}:$Y_2Si_2O_7$ nanopowders in the 1425-1675 nm wavelength range at room temperature when excited with diode laser operating at 800 nm. The spectral intensity of the lines and band broadening of the spectral output decreased with the increase of Er^{3+} mole concentration (Fig. 3a, 3b). The sample doped with 1.0 mole % Er^{3+} ions portrayed higher luminescence intensity than the other concentrations of Er^{3+} ions for each phase. The change in intensity with Er^{3+} concentration could be on account of the interaction among the Er^{3+} ions causing the energy transfer mechanisms.

Each spectrum contains an emission band with the strongest emission peak at about 1550 nm which correspond to the transition from the $^4I_{13/2}$ to the ground level ($^4I_{15/2}$), within the 4f shell of the Er^{3+} ions. The J-manifolds of Er^{3+} ions are split due to the low symmetry (C_1 or C_2) of the $Y_2Si_2O_7$ cation sites [25]. We observed that the spectral form and the count of the Stark components showed similar behavior for each Er^{3+} ions transitions in the powders at each phase. This phenomenon can be ascribed to the crystal field effect of ligand ions surrounding the Er^{3+} ions due to the same crystalline phase.

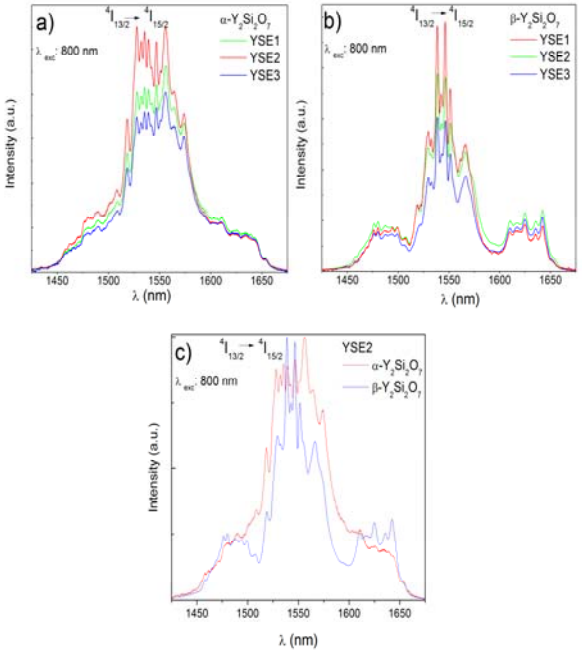

Figure 3. (a,b) The spectral output of lumınescence measurement of Er^{3+}:$Y_2Si_2O_7$ nanopowders in the 1425-1675 nm wavelength range at room temperature, **(c)** the comparison of emission bands for α- and β- Er^{3+}:$Y_2Si_2O_7$ 1% phases.

Figure 3c presents the comparison of emission bands for α and β- Er^{3+}:$Y_2Si_2O_7$ 1% phases. The spectral output of Er^{3+} emission shows strong dependency of the crystalline phase.

All these results can be attributed to the varied numbers of Y^{3+} (Er^{3+}) sites in the structures. In β-phase has one Y^{3+} site with C_2 symmetry and in α-phase there are four different Y^{3+} sites with C_1 symmetry. Er^{3+} ions can substitute in four different crystallographic sites of Y^{3+} ions in α-phase and emission from these four sites can occur in the widening of the emission band. Thus, the spectral output of the emission indicates a more significant difference of the silicate crystalline phase for Er^{3+} ions [25].

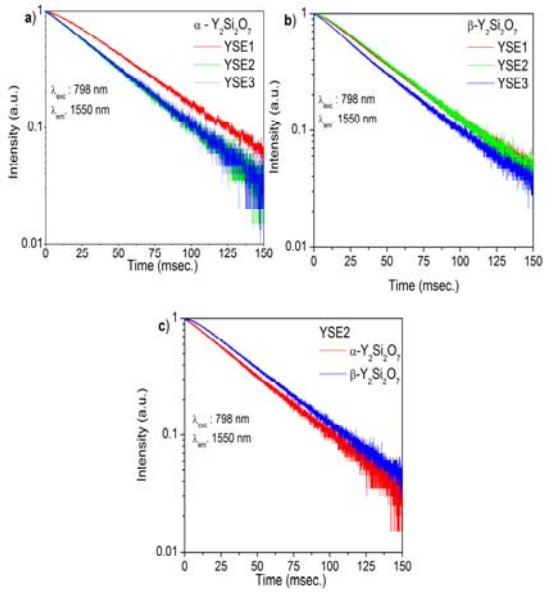

Figure 4. (a,b) The decay curves of the $^4I_{13/2}$ level for all samples under excitation wavelength of 798 nm at room temperature, **(c)** the comparison of decay curves for α-, and β- Er^{3+}:$Y_2Si_2O_7$ 1% phases.

The decay curves of the $^4I_{13/2}$ level have been measured for all samples excitation wavelength of 798 nm at room temperature. Figure 4 represents the decay plots in semi-log scale for three powders. The decay time of the $^4I_{13/2}$ emission decreases with increasing Er^{3+} mole concentration in the crystalline powders (Fig. 4a, 4b). The comparison of the PL decay curves of YSE2 sample in the three crystalline phases has been shown in Fig. 4c. All these decay curves of α- and β-phases have similar lifetime values.

4. Conclusion

α-$Y_2Si_2O_7$ and β-$Y_2Si_2O_7$ phosphors were successfully synthesized by sol-gel route using yttrium nitrate, erbium nitrate salts, TEOS (Si $(OC_2H_5)_4$) and hydrochloric acid as a catalyst for the hydrolysis of TEOS as the starting materials. The structure and the phase purity of the powders are determined by XRD and TEM analysis. α- and β-phases of crystalline Er^{3+}:$Y_2Si_2O_7$ phosphors were obtained via changing thermal treatment process.

The influences of cyristalline phase on the spectral profile of Er^{3+}:$Y_2Si_2O_7$ phosphors were studied in detail. Although doping of rare earth ion amounts do not contribute to the phase evolution of the powders, it is observed that the spectroscopic properties depend strongly on phase properties of $Y_2Si_2O_7$. We also observed that $Y_2Si_2O_7$: Er^{3+} 1.0 mol % showed higher PL intensity for each phase than the other concentrations of Er^{3+} ions.

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