Effect of Temperature and Boric Acid on the Photoluminescence Properties of SrIn$_2$O$_4$:Dy$^{3+}$ Material

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Abstract

Dy$^{3+}$ doped SrIn$_2$O$_4$ materials were prepared by a conventional solid state reaction. The synthesized materials were characterized using powder XRD and SEM. The synthesized materials were investigated using spectrophotometer at room temperature. It observed that two main bands peaking at (480-494) nm, 582 nm and of a weaker feature at (672-683) nm under 294 nm excitation. The effect of the sintered temperature and boric acid on the photoluminescence properties of the synthesized materials was studied in detail. The optimum sintered temperature and boric acid concentration was observed at 950°C and 0.02 mol, respectively. Finally, the photoluminescence spectra of the synthesized material SrIn$_2$O$_4$ with different Dy$^{3+}$ doping concentrations were analyzed at room temperature.

Keywords: Boric Acid, Luminescence, XRD, SEM, SrIn$_2$O$_4$

SrIn$_2$O$_4$:Dy$^{3+}$ Malzemelerinin Fotoluminesansı Özelliğine Borik Asit ve Sıcaklık Etkisi

Özet

Dy$^{3+}$ katkılı SrIn$_2$O$_4$ malzemeleri klasik kat hal reaksiyonu ile hazırlanmıştır. Sentezlenen malzemeler toz XRD ve SEM kullanarak karakterize edilmiştir. Sentezlenen malzemeler oda sıcaklığında bir spektrofluorometre kullanılarak araştırılmıştır. 294 nm ışığı altında (480-494) nm, 582 nm derdeki ana pik ve (672-683) nm’de zayıf bir pik gözlemlenmiştir. Sentezlenen malzemelerin fotoluminesans özellikleri sinterleme sıcaklığı ve borik asit ekisi detaylı olarak çalışılmıştır. Optimum sinterleme sıcaklığı ve borik asit konsantrasyonu sırasıyla 950°C ve 0.02 mol olarak gözlenmiştir. Son olarak da farklı konsantrasyonlar da Dy$^{3+}$ katkılı SrIn$_2$O$_4$ malzemelerinin fotoluminesansı ölçüldüğü oda sıcaklığında analiz edildi.

Anahtar Kelimeler: Borik Asit, Luminesans, XRD, SEM, SrIn$_2$O$_4$

1. Introduction

Among trivalent rare-earth elements, the Dysprosium ions have been incorporated into glasses and crystal lattices in order to obtain two primary color yellow/blue luminescent materials. Dy$^{3+}$-doped solid-state systems can be quite easily excited by the commercial UV or blue LEDs, because their excitation spectra exhibit several 4f–4f electronic bands located in the 340–480 nm spectral range [1]. Indium belongs to the same IIIA group of periodic table of elements with boron, aluminum and gallium and exhibits similar chemical properties. SrIn$_2$O$_4$, is an indium compound, is characterized by having an association SrO$_2$ polyhedra and InO$_6$ octahedra. It has excellent host lattice for efficient luminescence due to stable physical and chemical properties [2,3]. Up to now, many papers related with rare earth ions doped SrIn$_2$O$_4$ have been reported by different research groups [2-7]. To assist the sintering reaction, addition of boric acid as a flux is a popular method to accelerate the sintering reaction. So, boric acid are widely used as the flux for the conventional solid-state reaction because of its low melting point [8]. So, in this study, SrIn$_2$O$_4$: Dy$^{3+}$ phosphors with different mol ratios of B$^3+$/Dy$^{3+}$ were prepared by a conventional solid state reaction. The synthesized materials were characterized by using the powder X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). After synthesis and characterization of all synthesized SrIn$_2$O$_4$ materials, the photoluminescence properties of these phosphors were studied in detail using a spectrophotometer.

2. Experimental

SrIn$_2$O$_4$:B$^{3+}$/SrIn$_2$O$_4$:Dy$^{3+}$, B$^{3+}$ phosphors were prepared by a conventional solid state reaction. SrCO$_3$, In$_2$O$_3$, H$_2$BO$_3$ and Dy$_2$O$_3$ were used as starting materials. The raw materials were weighed according to the stoichiometric proportions. The starting materials were thoroughly mixed in ethanol and ground an agate mortar at room temperature. The solution was completely evaporated to dryness, and then the mixtures placed in alumina crucibles. First, the mixtures were pre-sintered in a muffle furnace at about 450 °C for 1 h in air. The obtained powders were thoroughly mixed and then heated up to 650 °C for 1 h in air. After milling, the powders were slowly heated up at final temperature (900-1200°C). After cooling to room temperature, yellow powders were obtained. The XRD structural analysis of B$^{3+}$ and Dy$^{3+}$ doped SrIn$_2$O$_4$ materials were performed on an X-ray Phillips X’Pert Pro equipped with Cu Kα (30 kV, 15 mA, λ = 1.54051 Å) radiation at room temperature. Scanning was generally performed between 10° and 90° 20. Measurement was made with 0.0330° step size at 25°C temperature. Observation of particle morphology was investigated by scanning electron microscope (Philips XL-30S FEI). The photoluminescence spectra were measured at room temperature with a Thermo Scientific Lumina fluorescence spectrometer equipped with a 150 W Xenon lamp.

3. Results and Discussion

3.1. XRD and SEM Analysis

Fig. 1 shows the XRD pattern of the synthesized phosphors prepared by a solid state reaction without boric acid at different sintered temperatures (900-1200°C). The crystal structure of SrIn$_2$O$_4$ was appeared at 900, 950, 1000, 1100 and 1200°C, which are in agreement with the JCPDS (17-0643). Fig. 2 shows the morphology of SrIn$_2$O$_4$ prepared by a solid state reaction without boric acid at 900, 950 and 1000°C. The SEM photographs of the synthesized SrIn$_2$O$_4$ exhibit particles of irregular luminescence to nearly spherical geometry with rounded corners and smooth grain interfaces. The grain size distribution is narrow, ranging from 1 to 5 micrometer.
Fig. 1. XRD pattern of the synthesized phosphors prepared by a solid state reaction with different sintered temperatures.

Fig. 2. SEM photographs of SrIn$_2$O$_4$ particles prepared by a solid state reaction

a) 900°C  
b) 950°C  
c) 1000°C
3.2. Photoluminescence Properties of SrIn₂O₄:Dy³⁺

The excitation and emission spectra of SrIn₂O₄:Dy³⁺ are demonstrated in Fig. 3a and 3b. The excitation spectrum of SrIn₂O₄:Dy³⁺ (Fig. 3a) monitored with 582 nm emissions of Dy³⁺ (⁴F₉/2 → ⁶H₁₅/₂). Dy³⁺ with ⁴f⁹ configuration has complicated f-block energy levels, therefore various possible transitions between these levels are highly selective, and show sharp line spectra [9, 11, 12]. The weak bands in the range of 350–475 nm is ⁴f → ⁴f transitions of Dy³⁺, while a strong band about 294 nm can be attributed to a charge transfer band (CTB) of Dy³⁺–O₂⁻ [9, 13–15]. The emission spectrum of SrIn₂O₄:Dy³⁺ (Fig. 3b) has been measured upon 294 nm excitation. It consists of two main bands peaking at (480–494) and 582 nm and of a weaker feature at (672–683) nm. These are assigned to the transitions from the ⁴F₉/2 to the ⁶H₁₅/₂, ⁶H₁₃/₂ and ⁶H₁₁/₂ states, respectively [7, 9, 10, 16–20]. And the intensity of yellow (⁴F₉/2 → ⁶H₁₃/₂) emission is much stronger than that of blue (⁴F₉/2 → ⁶H₁₅/₂) emission [9, 16–19].

In addition, the emission and excitation spectra of the synthesized material SrIn₂O₄ with different Dy³⁺ doping concentrations were analyzed at room temperature. The dependence of the emission intensity on the Dy³⁺ concentration for the Sr₁₋ₓDyₓIn₂O₄ (0.0025 ≤ x ≤ 0.05) is shown in Fig. 4. The shapes and positions of the emission peaks have exhibited no obvious changes. With increasing Dy³⁺ concentration in SrIn₂O₄, the emission intensity of the synthesized phosphors increases and reaches a maximum at 0.005 mol. And then, when the mole concentration of Dy³⁺ ion exceeds this concentration level, the emission intensity decreases, due to concentration quenching. The concentration quenching of Dy³⁺ in phosphors is mainly caused by cross-relaxation, i.e., energy transfers from one Dy³⁺ to another neighbor Dy³⁺ by transition that match in energy [13, 21, 22]. Therefore, it can be seen that the optimum concentration of Dy³⁺ in SrIn₂O₄ is 0.005 mol.

Fig. 3. The excitation (a) and emission (b) spectra of SrIn₂O₄:Dy³⁺(1%) phosphor prepared by a solid state reaction at 950°C (λ_{exc}=294nm, λ_{em}=582 nm).

Fig. 4. Emission spectra of Dy³⁺ (0.25, 0.50, 0.75, 1, 2, 3, 4, and 5 mol%): SrIn₂O₄ phosphors (λ_{exc}=294 nm) prepared by a solid state reaction at 950°C.
3.3. Influence of Boric Acid

Recently, the effect of boric acid on the luminescence properties has been extensively investigated by the scientists. They were observed that the emission intensity of various phosphors was significantly increased when the minor amount of boric acid was added to the hosts [23-31]. So, the emission spectra of SrIn$_2$O$_4$:Dy$^{3+}$ with different B$^{3+}$ doping concentrations were analyzed at room temperature. The molar ratio of H$_3$BO$_3$ to SrCO$_3$ was varied from 0 to 0.05. The effect of boric acid on the crystal structure of phosphors prepared by solid state reaction is shown Fig. 5. It is evident that phosphors showed that all the peaks were due to SrIn$_2$O$_4$ phase and no other crystalline phase could be detected with the increasing of the amount of boric acid.

Fig. 5. XRD patterns of the synthesized SrIn$_2$O$_4$:Dy$^{3+}$ (1%) phosphors with different amount of boric acid

Fig. 6 further shows the emission intensity as a function of the B$^{3+}$. The emission intensity increases with the H$_3$BO$_3$ content, reaching a maximum at H$_3$BO$_3$ content of x =0.02, and then decreases at higher H$_3$BO$_3$ content. The introduction of a small amount of H$_3$BO$_3$ to enter the lattice sites, meaning that more Dy$^{3+}$ helps Dy$^{3+}$ to emit light. Moreover, it increases the radiative transition probability. Therefore, the emission is finally intensified with the introduction of a small amount of H$_3$BO$_3$, although the non-radiative transition probability increases. However, when H$_3$BO$_3$ content exceeds 0.02 mol, non-radiative energy transfers will result in the luminescence quenching [24]. It can be express that the optimum molar ratio of boric acid to strontium carbonate is about 0.02.

Fig. 6. The emission spectra of SrIn$_2$O$_4$:Dy$^{3+}$ (1%) with different amount of boric acid ($\lambda_{ex}$=294 nm, 950ºC)
3.4. Influence of Sintered Temperature

Until recently, the effect of sintered temperature on the photoluminescence properties has been extensively investigated by the scientists. They were observed that the emission intensity changes significantly with the increase in temperature [28-31]. So, the emission properties of $\text{SrIn}_2\text{O}_4:\text{Dy}^{3+}$ phosphor prepared at different sintered temperatures were analyzed. Fig. 7 shows the emission spectra of $\text{SrIn}_2\text{O}_4:\text{Dy}^{3+} (92\%)$ phosphor with different sintered temperatures in the range 900-1200°C under the excitation of 294 nm. With increasing the sintered temperature, the emission intensity of $\text{SrIn}_2\text{O}_4:\text{Dy}^{3+}$ increased up and reached a maximum at 950°C. When the sintered temperature exceeded 950°C, the emission intensity of the synthesized phosphor decreased. The phosphors prepared at 950°C have high photoluminescence intensity because of fine crystallinity that can be seen in Fig. 1. It is obvious that the emission intensity increased with the decrease of the sintered temperature, due to the improvement of crystallinity which is well in agreement with Fig. 1. However, the emission intensity changes significantly with the increase in temperature until 1200°C at which the emission intensity gets very low, it may be due to excessive sintering and aggregation of particles.

4. Conclusions

Dy$^{3+}$ doped SrIn$_2$O$_4$ materials were prepared by a conventional solid state reaction. The synthesized materials were characterized using powder XRD and SEM. The XRD pattern of all synthesized phosphors is in agreement with the JCPDS (17-0643). The synthesized materials were investigated using spectrofluorometer at room temperature. It observed that two main bands appearing at (480-494) nm, 582 nm and of a weaker feature at (672-683) nm under 294 nm excitation. The effect of the sintered temperature and boric acid on the photoluminescence properties of phosphors was studied in detail. With introduction of boric acid (0.02 mol), the emission intensity can be enhanced by 1.5 times under 294 nm excitation. And, optimal photoluminescent properties was observed at the sintering temperature of 950°C due to fine crystallinity. Also, the dependence of the emission intensity on the Dy$^{3+}$ concentration for the SrIn$_2$O$_4$ was studied in detail. It was observed that the concentration quenching of Dy$^{3+}$ in SrIn$_2$O$_4$ is 0.005 mol.

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References

11. Nagpure I. M., Shinde K. N., Dhole S. J., Kumar A., Photoluminescence characterization of Dy$^{3+}$ and Eu$^{3+}$ ion in Mg$_2$(PO$_4$)$_2$F (M = Ba, Sr, Ca) phosphors, Journal of Alloys and Compounds, (481), 632-638, 2009.


