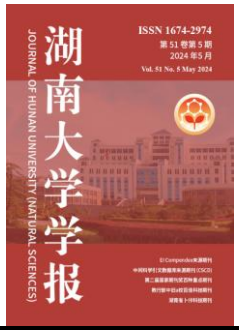

湖南大学学报（自然科学版）
Journal of Hunan University (Natural Sciences)

第 51 卷 第 5 期
2024 年 5 月

Available online at http://jonuns.com/index.php/journal/index

Vol. 51 No. 5
May 2024

Open Access Article

https://doi.org/10.55463/issn.1674-2974.51.5.6

Sol-Gel Synthesis and Characterization of Cerium-Doped Yttrium Silicate

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Received: February 18, 2024 / Revised: March 10, 2024 / Accepted: April 14, 2024 / Published: May 30, 2024

Abstract: A $(Y_{0.995}Ce_{0.005})2SiO_5$ ceramic phosphor was prepared using the sol-gel method. The starting raw materials were yttrium nitrate hexahydrate, cerium nitrate hexahydrate, and tetraethyl orthosilicate. The obtained sol was dried at 70°C to form a gel that was thermally treated at different temperatures up to 1400°C with a hold of 2 h at the maximum temperature. The synthesized powders were characterized using XRD, SEM, EDS, and luminescence analyses. At up to 800°C, the synthesized product is amorphous. At 1000°C, the predominant phase is Y_2SiO_5-X1, and there is a small amount of phase $Y_{4.67}(SiO_4)_3O$. At 1200°C, the phases Y_2SiO_5–X2 (PDF #36-1476), $Y_{4.67}(SiO_4)_3O$, and some Y_2O_3 are evident. At 1400°C, Y_2SiO_5–X2 becomes the main phase together with a small amount of the $Y_2Si_2O_7$ phase. SEM and EDS confirm the XRD results for the synthesized Y_2SiO_5-X2 phase at 1400°C. The SEM image reveals particles ranging in size from 1 to 5 microns, displaying irregular to spherical shapes. These particles are observed to be interconnected in agglomerates. EDS indicates that it contains 25.51-wt.% SiO_2, 72.32-wt.% Y_2O_3, and 2.17-wt.% CeO. At 1400°C, the resulting ceramic phosphor $Y_2SiO_5:Ce^{3+}$ exhibits photoluminescence emission peaks at 263, 301, and 356 nm at λ excitation of a 433-nm wavelength. The aim of the present study is the low-temperature synthesis of cerium-doped ceramic phosphor with potential application as an additive in glasses for dental glazes for application on zirconium dental implants to increase the fluorescent and luminescent properties of the same.

Keywords: sol-gel synthesis, cerium-doped yttrium silicate, Y_2SiO_5-X2 phase, ceramic phosphor.

铈掺杂硅酸钇的溶胶-凝胶合成及表征

摘要：采用溶胶-凝胶法制备(Y0.995Ce0.005)2SiO5 陶瓷荧光粉。起始原料为硝酸钇六水合物、硝酸铈六水合物和四乙基正硅酸盐。将所得溶胶在 70 摄氏度下干燥以形成凝胶，然后在最高温度 1400 摄氏度下进行不同温度热处理，在最高温度下保持 2 小时。使用 XRD、扫描电子显微镜、能谱分析和发光分析对合成粉末进行表征。在高达 800 摄氏度的温度下，合成产物为无定形。在 1000 摄氏度时，主要相为 Y2SiO5-X1，并有少量相 Y4.67(SiO4)3O。在 1200 摄氏度时，可明显看到相 Y2SiO5–X2 (PDF #36-1476)、Y4.67(SiO4)3O 和一些 Y2O3。在 1400 摄氏度时，Y2SiO5–X2 成为主要相，并伴有少量 Y2Si2O7 相。扫描电子显微镜和能谱分析 证实了 1400 摄氏度时合成的 Y2SiO5-X2 相的 XRD 结果。扫描电子显微镜图像显示颗粒大小从 1 到 5 微米不等，呈不规则到球形。观察到这些颗粒在团聚体中相互连接。能谱分析表明它含有 25.51 重量%二氧化硅、72.32 重量%

氧化钇和 2.17 重量％ CeO。在 1400 摄氏度时，所得陶瓷荧光粉 Y2SiO5:Ce3+在 433 纳米波长的 λ 激发下在 263、301 和 356 纳米处表现出光致发光发射峰。本研究的目的是低温合成掺铈陶瓷荧光粉，其可能作为牙科釉料玻璃的添加剂应用于锆牙科植入物，以提高其荧光和发光性能。

关键词：溶胶-凝胶合成，掺铈硅酸钇，Y2SiO5-X2 相，陶瓷荧光粉。

1. Introduction

Rare earth-doped phosphors are the focus of current research activities and have been successfully applied in field emission displays (FEDs), luminescent glasses, glazes, paints, 3D display technology, white light-emitting devices, and others [1-2]. Rare earth-doped phosphors are photoluminescent materials. Photoluminescent materials exhibit high sensitivity when exposed to light. At a certain wavelength, they absorb light, and the absorbed light is emitted at a different wavelength. This radiation is usually visible light [3-5]. Ceramic phosphors are primarily utilized in LED devices [1]. They are also introduced as additives in small quantities in glasses used for glazes on dental ceramics made from zirconium oxide to improve the luminescence and color characteristics of dental crowns and prostheses [2, 3]. Yttrium silicate is commonly used as a host for several “rare earth dopants” such as Ce, Eu, Lu, Tb, Pr, and Yb. Ce-activated Y2SiO5 is one of the most popular low-voltage blue phosphors in field emission displays (FEDs) because of its excellent luminescence efficiency, color purity, and high thermal stability [4-10]. The luminescence in Y_2SiO_5:Ce arises because of a characteristic transition (Ce creates intermediate energy levels within the wide band gap, facilitating the transition from 5d to 4f.). The photoluminescence capabilities of Ce3+ ions in Y2SiO5 nanocrystals are influenced by the size and structure of the crystals. The smaller and more spherical the particles, the better their luminescence characteristics. To obtain particles with these properties, it is necessary to apply the sol-gel method, in which the ceramic phosphorus is synthesized at a lower temperature than in the solid-phase synthesis [4-10].

Cerium-doped yttrium silicate has two different monoclinic crystal structures: the X1 phase with space group P 21/c and the X2 phase with space group B 2/c. In each of these two phases, there are two possible Y sites in the Y_2SiO_5 matrix because of the different coordination numbers [8, 9]. The activator Ce (radius of 0.106 nm) can easily replace Y (radius of 0.93 nm) during the synthesis process and therefore leads to two different crystallographic sites for Ce in Y_2SiO_5 [10]. Yttrium silicate in the X2 phase is obtained at a high temperature above 1500°C when solid-phase synthesis is performed. Therefore, other methods are sought to synthesize Y_2SiO_5:Ce with a structure of Y_2SiO_5–X2 at a lower temperature. The sol-gel method is a suitable method in which the synthesis temperature is lowered below 1500°C and the particle size is reduced [11-14].

Enhancing the fluorescent and luminescent properties of dental glazes is crucial for their effectiveness. Our innovative approach involves incorporating a cerium-doped ceramic phosphor synthesized by us, known for its exceptional luminescent properties. This addition aims to elevate the quality of dental glazes.

The aim of this article is the sol-gel synthesis of a $(Y_{0,995}Ce_{0,005})_2SiO_5$ ceramic phosphor at a lower temperature compared with solid-phase synthesis and the characterization of the obtained product by XRD, SEM, EDS, and PL.

2. Experiment

2.1. Methodology

The methodology of the experiment consists of the calculation of the starting raw materials for the synthesis of yttrium silicate with the addition of cerium oxide, a sol-gel process from the starting raw materials, in this case nitrates and TEOS, drying at 70°C, heat treatment at different temperatures to follow the phase changes and obtaining Y_2SiO_5-X2 (PDF #36-1476) phase at the lowest possible temperature, which is distinguished by good luminescent properties.

For the sol-gel synthesis of 10 g $(Y_{0.995}Ce_{0.005})_2SiO_5$ powder, the necessary amounts of raw materials were calculated. 26.5 g of $Y(NO_3)_3.6H_2O$ (99.9%, Alfa Aesar), 0.155 g of $Ce(NO_3)_3.6H_2O$ (99.0%, Fluka), and 7.3 g of TEOS (99.0%, Fluka). Nitrates were previously dissolved separately in ethyl alcohol. TEOS was mixed with ethyl alcohol and water, and HCl was added to accelerate hydrolyzation and to adjust the pH to 1-2. Subsequently, the solution of the nitrate and pre-hydrolyzed TEOS was stirred on a magnetic stirrer for 45 min. The final step of the synthesis was the addition of ammonia, which increased the pH to neutral. The resulting sol was dried in an oven at 70°C to obtain a gel. The resulting gel is then thermally treated at different temperatures (400°C, 600°C, 800°C, 1000°C, 1200°C and 1400°C) with a 2-h hold at the maximum temperature.

2.2. Sample Characterization

The powders obtained were analyzed using X-ray powder diffractometry with a PANalytical Empyrean diffractometer system. This system features a goniometer radius of 240 mm, operates at 40 kV and 30 mA, and utilizes CuKa radiation. Additionally, it is equipped with a 3D-pixel detector. Furthermore, the particle morphology was observed using a SEM "JEOL JCXL-733 - Japan". The SEM was coupled with an EDS LINK 10/85 – Japan to analyze the elemental composition of the particles. The photoluminescence (PL) of the ceramic phosphor was measured using a spectrofluorometer, FluoroLog 3-22.

3. Results and Discussion

As shown in Fig. 1, it was proved by XRD that the obtained powder is amorphous at up to 800°C. As the thermal treatment temperature increases, crystalline phases form.

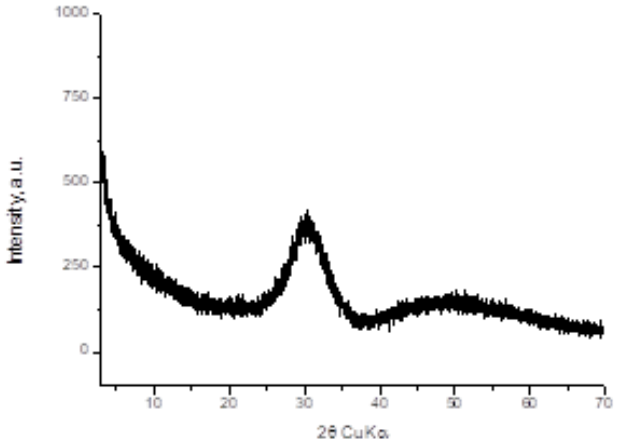


Fig. 1 XRD analysis of $(Y_{0.995}Ce_{0.005})_2SiO_5$ powder synthesized using the sol-gel method and thermally treated at 800°C with a 2-h hold at the maximum temperature (The authors)

Fig. 2 shows that at 1000°C, the predominant phase is Y_2SiO_5-X1 (PDF #04-014-7484) and a small amount of $Y_{4.67}(SiO_4)_3O$ phase (PDF #30-1457).

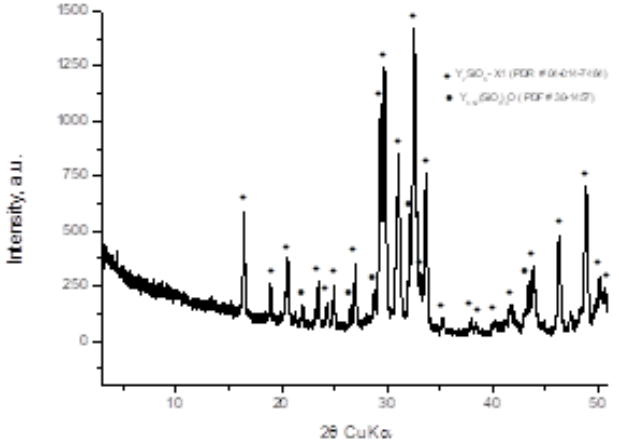


Fig. 2 XRD analysis of $(Y_{0.995}Ce_{0.005})_2SiO_5$ powder synthesized using the sol-gel method and thermally treated at 1000°C with a 2-hour hold at the maximum temperature (The authors)

At 1200°C, the phases Y_2SiO_5-X2 (PDF #36-1476), $Y_{4.67}(SiO_4)_3O$ (PDF #30-1457), and some Y_2O_3 are evident, as shown in Fig. 3.

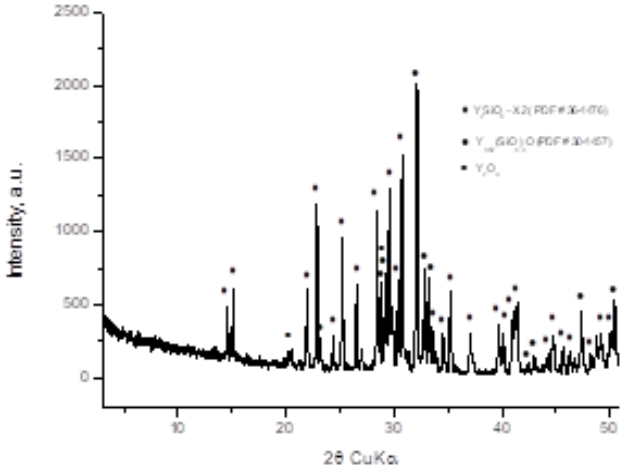


Fig. 3 XRD analysis of $(Y_{0.995}Ce_{0.005})_2SiO_5$ powder synthesized using the sol-gel method and thermally treated at 1200°C with a 2-hour hold at the maximum temperature (The authors)

At 1400°C, we already have an almost single-phase synthesis of Y_2SiO_5–X2 (PDF #36-1476) and minimal presence of $Y_2Si_2O_7$ (#38-0440), as shown in Fig. 4.

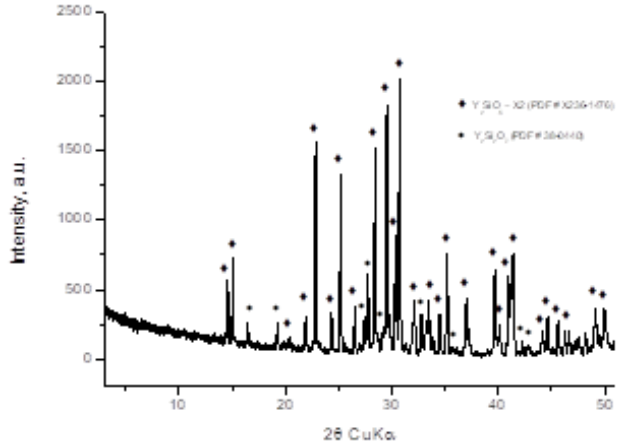
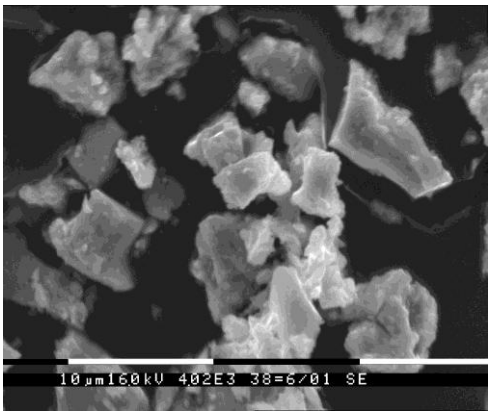


Fig. 4 XRD analysis of $(Y_{0.995}Ce_{0.005})_2SiO_5$ powder synthesized using the sol-gel method and thermally treated at 1400°C with a 2-hour hold at the maximum temperature (The authors)

SEM was used to study the morphology of Y_2SiO_5:Ce powder obtained after thermal treatment at 1000°C and 1400°C for 2 h at maximum temperature.

Fig. 5 shows SEM of $(Y_{0,995}Ce_{0,005})2SiO_5$ powder after thermal treatment at 1000°C for 2 h at maximum temperature. It is observed particles with an irregular and monoclinic shape, with sizes ranging from 1 to 10 mμ.



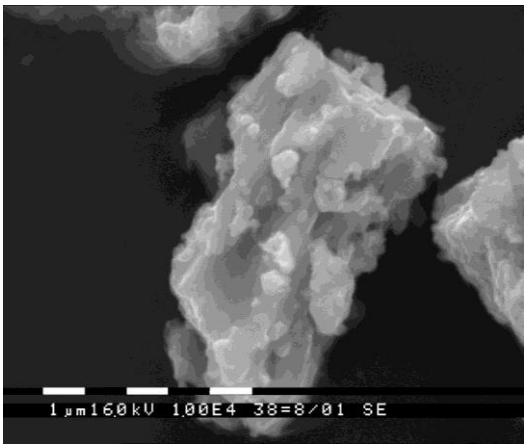
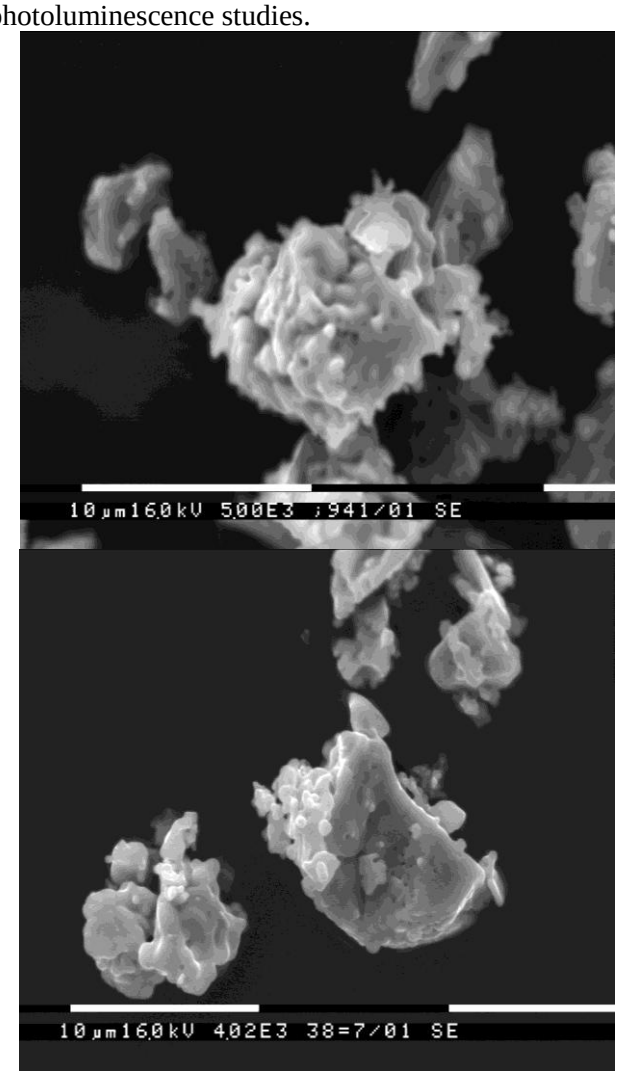


Fig. 5 SEM images of $(Y_{0.995}Ce_{0.005})_2SiO_5$ powder synthesized using the sol-gel method and thermally treated at 1000°C with a 2-hour hold at the maximum temperature (The authors)

At 1400°C, particles with irregular to spherical shapes with sizes between 1 and 5 mμ are observed, which are connected in agglomerates. As seen in Fig. 6, which shows the SEM of the $(Y_{0.995}Ce_{0.005})_2SiO_5$ powder thermally treated at 1400°C. EDS of Y_2SiO_5-X2 (PDF #36-1476) phase shows the following average content: SiO_2 – 25.51 wt.%, Y_2O_3 – 72.32 wt.%, and CeO – 2.17 wt.%. Ce-doped Y_2SiO_5 powder obtained at 1400°C was further characterized by photoluminescence studies.



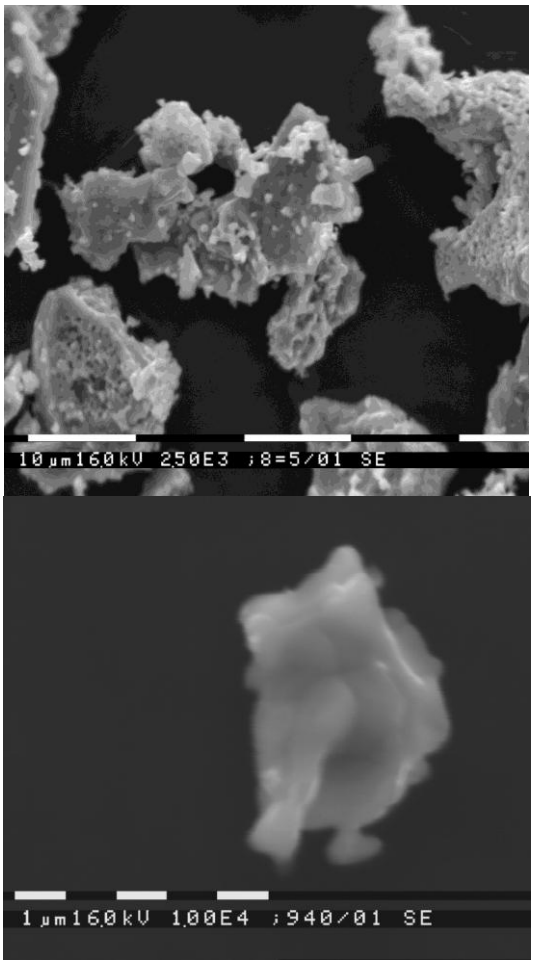


Fig. 6 SEM images of (Y0.995Ce0.005)2SiO5 powder synthesized using the sol-gel method and thermally treated at 1400°C with a 2-hour hold at the maximum temperature (The authors)

Using the low-temperature sol-gel method, (Y0.995 Ce0.005)2SiO5 was synthesized at a lower temperature of 1400°C, mainly containing the crystalline phase Y2SiO5-X2 (PDF #36-1476), with particles with irregular to spherical shapes with sizes between 1 and 5 mμ which is characterized by luminescent properties.

Fig. 7 and 8 show the excitation (PLE) and emission (PL) spectra of $Y_2SiO_5:Ce^{3+}$ phosphor samples prepared by the sol-gel method and calcined at 1400°C for 2 h at maximum temperature.

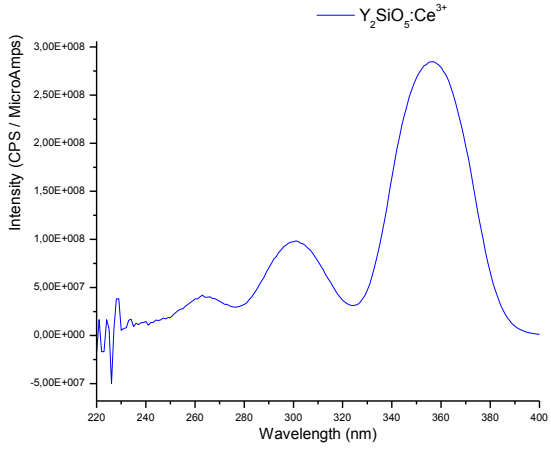


Fig. 7 PL excitation spectrum at λ of 433-nm emission of Y_2SiO_5:Ce phosphor powder (The authors)

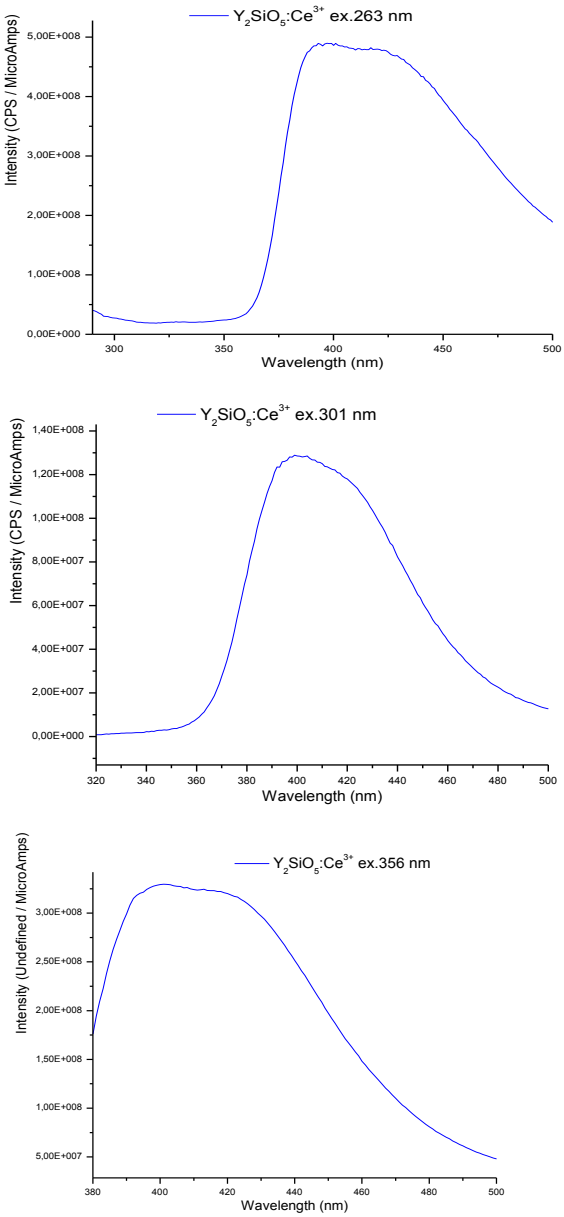


Fig. 8 PL emission spectra at λex 263, 301, and 356 nm (The authors)

The excitation spectra consist of three bands with maxima at 263, 301, and 356 nm, corresponding to the transitions from the ground state F to d states in Ce^{3+}.

4. Conclusion

Cerium-doped ceramic phosphor is produced at high temperatures by solid-phase synthesis. In our study, we obtained the same at a low temperature of 1400°C. By the sol-gel method, yttrium silicate doped with cerium $(Y_{0.995}Ce_{0.005})_2SiO_5$ was obtained from the raw materials yttrium nitrate hexahydrate, cerium nitrate hexahydrate, and tetraethyl orthosilicate. The resulting powders were thermally treated at different temperatures up to 1400°C with a 2-h hold at the maximum temperature and characterized by XRD, SEM, EDS, and photoluminescence analysis. At up to 800°C, the synthesized product is amorphous. At 1000°C, the predominant phase is Y_2SiO_5-X1 (PDF 04-014-7484), and there is a small amount of phase $Y_{4.67}(SiO_4)_3O$ (PDF #30-1457). At 1200°C, the phases Y_2SiO_5-X2 (PDF #36-1476), $Y_{4.67}(SiO_4)_3O$ (PDF #30-1457), and some Y_2O_3 are evident. At 1400°C, Y_2SiO_5-X2 (PDF #36-1476) becomes the main phase together with a small amount of the $Y_2Si_2O_7$ (PDF 38-0440) phase. SEM and EDS confirm the XRD results for the synthesized Y_2SiO_5-X2 phase at 1400°C. The ceramic phosphor $Y_2SiO_5:Ce^{3+}$ was successfully synthesized at 1400°C, resulting in particles that range in size from 1 to 5 microns and exhibit irregular to spherical shapes. These particles are bound together in agglomerates. EDS shows that they contain 25.51-wt% SiO_2, 72.32-wt% Y_2O_3, and 2.17-wt% CeO. The $Y_2SiO_5:Ce^{3+}$ ceramic phosphor obtained at 1400°C shows photoluminescence emission peaks at 263, 301, and 356 nm under λ excitation at a wavelength of 433 nm.

The synthesized ceramic phosphor will be utilized in upcoming experiments as an additive in glazes for dental zirconia ceramics, enhancing their color and esthetic characteristics.

Acknowledgment

This study was funded by the European Union - NextGenerationEU through the National Recovery and Resilience Plan of the Republic of Bulgaria, Project No. BG-RRP-2.004-0002 “BiOrgaMCT.”

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