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# COMPARATIVE STUDY OF THE SYNTHESIS AND PHOTO-PHYSICAL CHARACTERISTICS OF A NEW BLUE-EMITTING NANOCRYSTAL FOR NUV-EXCITED LEDS

## PRIMERJALNA ŠTUDIJA SINTEZE IN OPTIČNO-FIZIKALNIH ZNAČILNOSTI NOVIH MODRO SEVAJOČIH NANOKRISTALOV ZA Z NUV VZBUJANIH LED

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In this research, a new blue-emitting nanocrystalline phosphor, $SrZn_2Si_2O_7$: $Eu^{2+}$, utilizable in InGaN LEDs, was successfully synthesized via two routes: the sol-gel method (SG) and solid-state reaction (SS). The effects of the preparation processes on the crystallization, morphology and thermal properties were analyzed by appropriate techniques, such as thermogravimetric-differential thermal analysis (TG-DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The sample synthesized by the wet chemical method has a relatively regular morphology, a higher phase purity and a crystallite size of approximately 30 nm. Furthermore, luminescence spectrophotometry was performed for the investigation of the optical characteristics. The obtained phosphors emit blue light due to the $4f^65d^1(^2D) \rightarrow 4f^7(^8S_{7/2})$ transition of the $Eu^{2+}$ ions, which act as luminescence centers in the host lattice. After the excitation in the near-UV region, the phosphors prepared by SG have a higher emission intensity with a color coordination of $x = 0.176$, $y = 0.193$.

Keywords: synthesis, nanocrystalline, luminescence, functional materials, photonic devices

V tej raziskavi je bil uspešno sintetiziran nov, modro sevajoč nanokristalni fosfor $SrZn_2Si_2O_7$: $Eu^{2+}$, uporaben v InGaN LED, po dveh metodah: po sol-gel-metodi (SG) in reakciji v trdnem (SS). Učinek postopka priprave na kristalizacijo, morfologijo in termične lastnosti je bil analiziran s primernimi tehnikami, kot je termogravimetrična diferenčna termična analiza (TG-DTA), rentgenska difrakcija (XRD) in vrstična elektronska mikroskopija (SEM). Vzorec, sintetiziran z mokro kemijsko metodo, ima relativno pravilno morfologijo, veliko čistost faze in velikost kristalov okrog 30 nm. Izvršena je bila tudi luminiscenčna spektrofotometrija za preiskavo optičnih značilnosti. Dobljeni fosforji so emitirali modro svetlobo zaradi $4f^65d^1(^2D) \rightarrow 4f^7(^8S_{7/2})$-prehoda $Eu^{2+}$ ionov, ki učinkujejo kot centri luminiscence v gostujoči rešetki. Po vzbujanju blizu področja UV so imeli fosforji, pripravljeni po SG-metodi, višjo intenziteto emisije s koordinacijo barve $x = 0{,}176$, $y = 0{,}193$.

Ključne besede: sinteza, nanokristaliničnost, luminiscenca, funkcijski materiali, fotonske naprave

## 1 INTRODUCTION

In recent years, light-emitting diodes (LEDs) have emerged as a prominent class of lighting devices and the study of RGB phosphors suitable for near-ultraviolet (NUV) excitation has been attracting more and more attention for fabricating white LEDs.[1,2] LEDs have a great potential to replace conventional lighting sources, like incandescent and fluorescent lamps, due to their many favorable characteristics, such as a long lifetime and environment-friendly properties.[3,4] The new developments in the field of optical materials are the search for ideal/suitable phosphors for the conversion of the NUV emission from InGaN chips into visible light. Among the different sorts of these materials, silicate phosphors have attracted researchers' attention because of the advantages of a stable crystal structure, stability to high irradiation powers, etc.[5,6] In general, various preparation methods may greatly affect the crystallization, morphology, particle size and optical characteristics of phosphor materials. Compared with samples obtained by the conventional SS route, the phosphor materials synthesized by the wet chemical method have advantages such as a low calcination temperature, good mixing of the starting materials and a higher uniformity of the particle size distribution.[7–9] But from another point of view, the solid state as the most convenient method has industrial possibilities. In order to optimize the characteristics of $SrZn_2Si_2O_7$: $Eu^{2+}$, in this study, two experimental methods, SS and SG, were used to prepare the nanocrystalline phosphors and the effects of the preparation processes on the crystallization, morphologies, and optical properties were investigated.

## 2 EXPERIMENTAL METHOD

$Sr_{0.96}Zn_2Si_2O_7$:$0.04Eu^{2+}$ samples were synthesized using the SG and SS methods. TEOS and nitrate salts in SG and metal oxides and acid boric as a flux in the SS were used to prepare the precursors. Finally, the

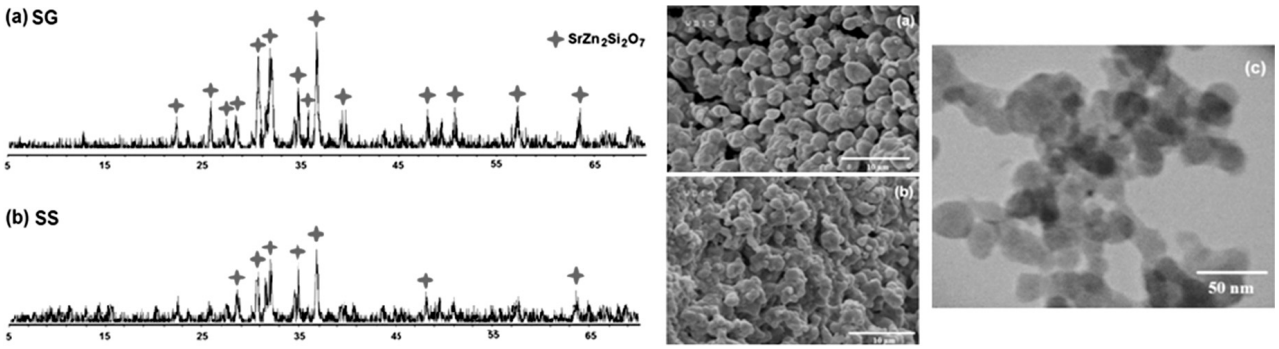


**Figure 1:** XRD patterns, SEM images and TEM micrograph of $SrZn_2Si_2O_7$: $Eu^{2+}$ prepared via different methods
**Slika 1:** XRD-posnetka, SEM-posnetka in TEM-posnetek $SrZn_2Si_2O_7$: $Eu^{2+}$, pripravljenega z različnimi metodami

precursors were calcined at 1100 °C for 1 h in a weak reductive atmosphere of flowing 5 % $H_2$–95 % $N_2$ gas. Also, in order to characterize the final phosphors, X-ray diffraction (XRD), scanning and transition electron microscopy (SEM/TEM), thermogravimetric-differential thermal analysis (TG-DTA), and fluorescence spectroscopy were used.

## 3 RESULTS AND DISCUSSION

The XRD patterns and the SEM micrographs of the samples synthesized with SG and SS are shown in **Figure 1**. The main phase can be indexed to the phase of $SrZn_2Si_2O_7$ for both samples (JCPDS 10-0051). From the diffraction intensity, it can be seen that the order of the crystallization and the microstructural regularity for the phosphor which were prepared via SG are higher than those of the SS due to the uniformity of the starting reactants, and thus this method is more favorable for the formation of superfine phosphors. Moreover, the TEM image depicts that the average size of the crystallites for the SG sample is about 30 nm.

The TG-DTA curves of the $SrZn_2Si_2O_7$ precursors were studied, as presented in **Figure 2**, to understand their pyrolysis behavior and crystallization process. The following chemical reactions could be inferred, during the synthesis of the two phosphors:[10,11]

**Sol-gel sample:**

**Reaction A:**
$2(Zn(NO_3)_2.6H_2O)$ (cryst) → 2ZnO (amorph) + $12H_2O$ + $4NO_2$ + $O_2$

**Reaction B:**
$Si(OH)_4$ (amorph) → $SiO_2$ (amorph) + $2H_2O$

**Reaction C:**
ZnO (amorph) → ZnO (Cryst)

**Reaction D:**
$2(Sr(NO_3)_2)$ (cryst) → 2SrO (amorph) + $4NO_2$ + $O_2$

**Reaction E:**
SrO (amorph) + $SiO_2$ (amorph) → $SrSiO_3$ (cryst.)
$SrSiO_3$ (cryst) + 2ZnO (cryst) + $SiO_2$ (amorph) → $SrZn_2Si_2O_7$ (cryst)

**Solid state sample:**

**Reaction A:**
$2H_3BO_3$ → $B_2O_3$ + $3H_2O$

**Reaction B:**
$SrCO_3$ → SrO (amorph) + $CO_2$

**Reaction C:**
SrO (amorph) + 2ZnO (amorph) + $2SiO_2$ (amorph) → $SrZn_2Si_2O_7$ (cryst)

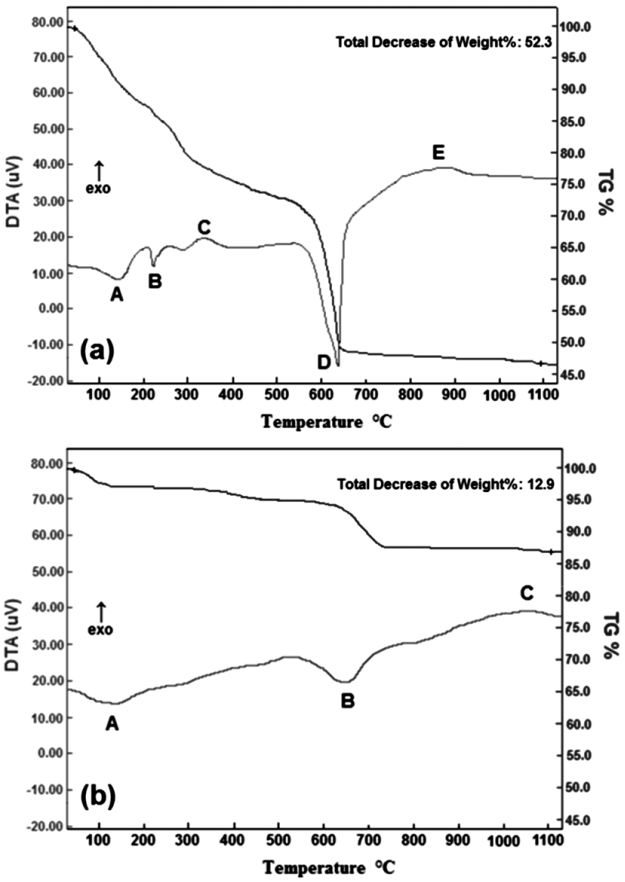


**Figure 2:** DTA and TG curves of $SrZn_2Si_2O_7$ gels from 25 °C up to 1150 °C for: a) SG and b) SS samples
**Slika 2:** DTA- in TG-krivulje gela $SrZn_2Si_2O_7$ od 25 °C do 1150 °C za: a) vzorce SG in b) vzorce SS

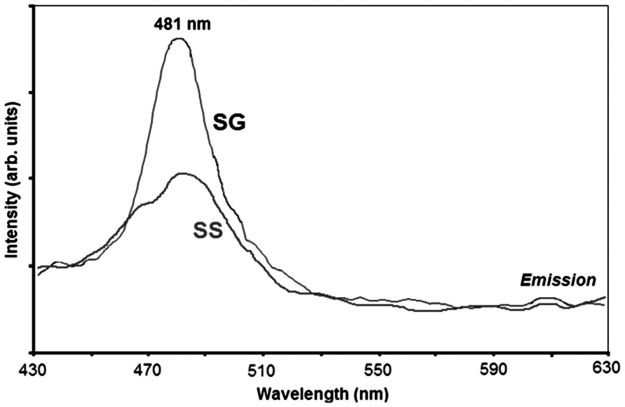


**Figure 3:** Emission spectra of $SrZn_2Si_2O_7$: $Eu^{2+}$ prepared via different methods

**Slika 3:** Emisijski spekter $SrZn_2Si_2O_7$: $Eu^{2+}$, pripravljen z različnima metodama

The effects of the different synthesis methods on the optical properties were also investigated. **Figure 3** shows the emission spectra of the $SrZn_2Si_2O_7$: $Eu^{2+}$ phosphors prepared by SG and SS. Under near-UV excitation the phosphors emit an intense blue light, peaking at 481 nm, with similar profiles because of the same composition and the same crystalline lattice, while the intensity is different, which is consistent with the degree of crystallization of the phosphors. The emission peak is attributed to a typical $4f^6 5d^1(^2D) \rightarrow 4f^7(^8S_{7/2})$ transition of $Eu^{2+}$ and for SG sample, the color coordination is ($x$ = 0.176, $y$ = 0.193). However, there is no special emission of $Eu^{3+}$ in these spectra, which implies that $Eu^{3+}$ ions have been reduced to $Eu^{2+}$ completely. Double or triple Eu ions can be present in ionic solids. For the case of the triple charged, all the 5*d* and 6*s* orbitals are empty and the 4*f* is partially occupied. The optically active 4*f* electrons are shielded from the crystalline electric field by the outer 5*s* and 5*p* shells. The resulting effect is that the neighboring ligands have very little affect on the 4*f* electrons. But for the case of the divalent Eu ions, the energy separation between the $4f^7$ and $4f^6 5d^1$ configurations will be large and these transitions are dipole-allowed, which are about $10^6$ times stronger than the very frequently observed $4f \rightarrow 4f$ transitions in trivalent Eu ions.[12] Therefore, a reducing atmosphere helps to reduce $Eu^{3+}$ to $Eu^{2+}$ ions for better optical properties.

## 4 CONCLUSION

In summary, blue-emitting phosphor $SrZn_2Si_2O_7$: $Eu^{2+}$ was synthesized via two methods, SS and SG, for LED applications. The reducing atmosphere helped the $Eu^{3+}$ ions to reduce to $Eu^{2+}$ and the $4f^6 5d^1(^2D) \rightarrow 4f^7(^8S_{7/2})$ transition of $Eu^{2+}$ caused the strong emission peak at about 480 nm for the sample prepared via the SG method. The results reveal that the sample synthesized by wet chemical method has a relatively regular morphology, a small particle size and a higher luminescence intensity.

## 5 REFERENCES

[1] X. Y. Sun, J. H. Zhang, X. Zhang, Y. S. Luo, X. J. Wang, J. Rare Earths, 26 (**2008**), 421
[2] F. Xiao, Y. N. Xue, Q. Y. Zhang, Physica B, 404 (**2009**), 3743
[3] K. Sakuma, N. Hirosaki, R. Xie, J. Lumin., 126 (**2007**), 843
[4] S. Yao, D. Chen, J. Opt. Laser Technol., 40 (**2008**), 466
[5] W. H. Hsu, M. H. Sheng, M. S. Tsai, J. Alloys Compd., 467 (**2009**), 491
[6] J. S. Kim, P. E. Jeon, J. C. Choi, H. L. Park, Solid-state Commun., 133 (**2005**), 187
[7] M. Pang, X. Liu, J. Lin, J. Mater. Res., 20 (**2005**), 2676
[8] R. P. Rao, J. Electrochem. Soc., 143 (**1996**), 189
[9] R. Balakrishnaiah, D. Kim, S. S. Yi, K. Jang, H. S. Lee, J. H. Jeong, Mater. Letters, 63 (**2009**), 2063
[10] G. A. El-Shobaky, A. S. Ahmed, G. A. Fagal, M. Mokhtar, Thermochim Acta, 319 (**1998**), 67
[11] P. V. Ravindran, B. B. Kalekar, K. V. Rajagopalan, C. G. S. Pillai, P. K. Mathur, J. Nucl. Mater., 317 (**2003**), 109
[12] G. Blasse, B. C. Grabmaier, Luminescent materials, Springer Verlag, Berlin 1994