

Sol–gel synthesis of RE³⁺-activated CaWO₄ phosphores

Artūras Žalga^{1*},

Rokas Sažinas¹,

Edita Garškaitė¹,

Aivaras Kareiva¹,

Tomas Bareika²,

Gintautas Tamulaitis²,

Remigijus Juškėnas³,

Rimantas Ramanaukas³

A series of red-emitting phosphores containing CaWO₄:RE (RE = Tb³⁺, Eu³⁺, Sm³⁺) was prepared by an aqueous sol–gel method using tungsten (VI) oxide, WO₃, calcium nitrate tetrahydrate, Ca(NO₃)₂·4H₂O, terbium oxide, Tb₄O₇, europium oxide, Eu₂O₃, and samarium oxide, Sm₂O₃ as starting materials. Synthesized ceramics were characterized using infrared spectroscopy (IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) measurements. The obtained results clearly show that only CaWO₄:Eu phosphor can be effectively excited under photoexcitation at 280, 360 and 460 nm and exhibits red emission in the vicinity of 620 nm.

Key words: CaWO₄ phosphores, sol–gel synthesis, lanthanide doping, photoluminescence

¹ Faculty of Chemistry, Vilnius University,
Naugarduko 24, LT-03225 Vilnius, Lithuania

² Institute of Materials Science and
Applied Research, Vilnius University,
Saulėtekio 9, LT-10222 Vilnius, Lithuania

³ Institute of Chemistry, A. Goštauto 9,
LT-01108 Vilnius, Lithuania

INTRODUCTION

Photoluminescence study of different crystalline multinary metal oxide ceramics, either pure or doped, mainly with rare earth ions such as Eu³⁺, Er³⁺, Nd³⁺ etc., revealed a considerable potential of these materials in optoelectronic applications [1, 2]. These compounds could be widely used as phosphores in cathode-ray tubes, field emission, vacuum fluorescent and electroluminescent displays as well as scintillators in X-ray and positron emission tomographs [1–5]. The specific luminescence behaviour of crystalline ceramics is highly sensitive to the initial composition of the host material, dopant or substituent concentration and processing conditions. The optical properties of trivalent rare-earth ions (RE³⁺) in tungstate materials with scheelite (CaWO₄) structure have been widely investigated [6–9], especially due to their attractive third-order nonlinear dielectric susceptibilities [10, 12]. It is well known that rare-earth elements can form a series of isomor-

phous tungstates with the general formula RE_x(WO₄)₃ [13]. Because of their attractive luminescence and structural properties, tungstates have been intensively studied and found applications in many fields such as lasers, fluorescent lamps, and scintillators during the last few decades. Tungstates can be divided into two groups with a different crystal structure: scheelites (CaWO₄, BaWO₄, SrWO₄, RE₂(WO₄)₃ and PbWO₄) and wolframites (MgWO₄, CdWO₄, ZnWO₄ and others) [13, 14]. Calcium tungstate CaWO₄ is a representative example of tungstates with the scheelite structure containing Ca²⁺ ions and WO₄²⁻ groups with the coordination number of eight for Ca²⁺ and four for W⁶⁺, and is considered to be a highly functional material due to its prominent luminescence properties. When excited by short-wavelength ultraviolet radiation, X-rays or cathode rays, CaWO₄ shows an efficient blue emission. Moreover, many researchers focused their attention on europium (III) and samarium (III) ions as luminescence centres in red light phosphores with excellent emission properties. Thus, CaWO₄, whether doped or substituted by rare-earth elements, is an important optical material which has already

* Corresponding author. E-mail: arturas.zalga@chf.vu.lt

attracted particular interest because of its practical applications such as laser host materials in quantum electronics and scintillators in medical devices [15–18].

Owing to such a wide and diverse application potential of CaWO_4 ceramics, new routes for the synthesis of pure and homogeneously doped calcium tungstate are highly desirable. To date, most of the efforts in preparation of doped calcium tungstate have been directed to single crystals, powders, and films of CaWO_4 :RE. Meanwhile, there are still only a few reports on the preparation of nano-sized doped CaWO_4 :RE. Such a situation has stimulated this work and motivated us to continue investigations towards the development of synthesis routes for the preparation of nano-sized CaWO_4 doped by rare-earth elements. The sinterability and physical properties of CaWO_4 doped by Tb^{3+} , Eu^{3+} , and Sm^{3+} ions synthesized in an aqueous sol–gel process were investigated in the present study.

EXPERIMENTAL

The phosphores CaWO_4 :RE were prepared by the aqueous nitrate–tartrate sol–gel route. The starting materials – europium oxide (Eu_2O_3 , 99.99%), samarium oxide (Sm_2O_3 , 99.99%), terbium oxide (Tb_4O_7 , 99.9%), tungsten oxide (WO_3 , 99.9%), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%) – were weighed according to the desired stoichiometric ratio. Nitric acid (HNO_3) and ammonia ($\text{NH}_3 \cdot 4\text{H}_2\text{O}$) were used as solvents and reagents to regulate the pH of the solutions. Tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, 99.5%) was used as a complexing agent.

In the sol–gel process, WO_3 was first dissolved in 25 ml of concentrated ammonia solution by stirring at 70–80 °C. Secondly, tartaric acid (TA) with a molar ratio of $\text{W} / \text{TA} = 0.25$, dissolved in a small amount of distilled water, was added with a continuous stirring during several hours at the same temperature. Next, the stoichiometric amount of calcium nitrate tetrahydrate dissolved in distilled water was mixed with the previous solution. To prevent precipitation, the excess of ammonia was neutralized with concentrated HNO_3 until the pH reached the value of ~ 1.0 . Afterwards, RE_2O_3 (where RE = Eu, Sm) or Tb_4O_7 oxide was added directly to the reaction mixture. Finally, the same amount of the aqueous solution of the complexing agent was repeatedly added to the reaction mixture to prevent crystallization of metal salts during the gelation process. The beaker with the solution was closed with a watch glass and left with continuous stirring for 60 min. The obtained clear solution was concentrated by slow evaporation at 80 °C in an open beaker. A yellow transparent gel formed after nearly 90% of the water had been evaporated under continuous stirring. After drying in an oven at 105 °C, fine-grained powders were obtained. The precursor gels were calcined for 5 h at 500 °C in alumina crucibles and reground carefully in an agate mortar. Since the gels are very combustible, slow heating (1 °C/min), especially between 150 and 300 °C, was found to be essential. After intermediate grinding the obtained powders were annealed for 1 h at 800 °C in air at ambient pressure.

The synthesized samples were characterized by X-ray powder analysis (D8 Bruker AXS powder diffractometer) using $\text{CuK}\alpha_1$ radiation. The spectra were recorded at the standard rate of 1.5 2θ / min. After pressing the samples into pellets with KBr ($\sim 1.5\%$), the infrared (IR) spectra were recorded with a Perkin–Elmer FT-IR Spectrum 1000 spectrometer. The scanning electron microscope (SEM) DSN 962 was used to study the surface morphology and microstructure of the ceramic samples. The photoluminescence spectra were recorded at room temperature using a Hamamatsu spectrometer PMA-11 with a CCD camera. The samples were excited at different wavelengths using three LEDs emitting at 460, 360, and 280 nm.

RESULTS AND DISCUSSION

The RE–Ca–W–O nitrate–tartrate gels were annealed at 800 °C to obtain the CaWO_4 :RE phase. The ceramic samples were characterized by XRD analysis. The XRD patterns of synthesis products are shown in Fig. 1. One can see that the calcination of the RE–Ca–W–O nitrate–tartrate

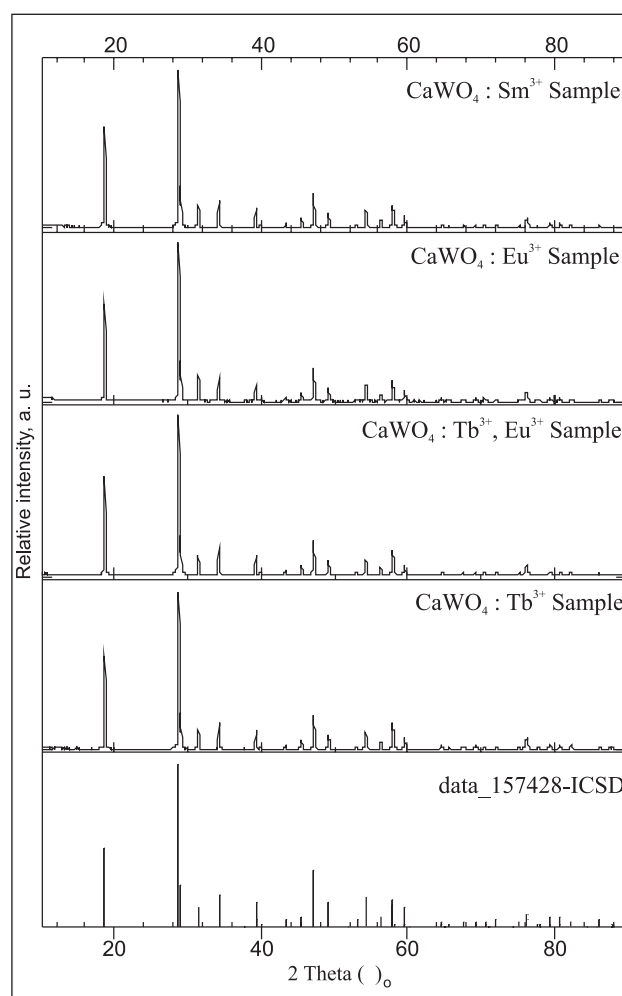


Fig. 1. X-ray diffraction patterns of RE^{3+} -ion-activated CaWO_4 samples sintered at 800 °C using tartaric acid as a complexing agent in sol–gel processing

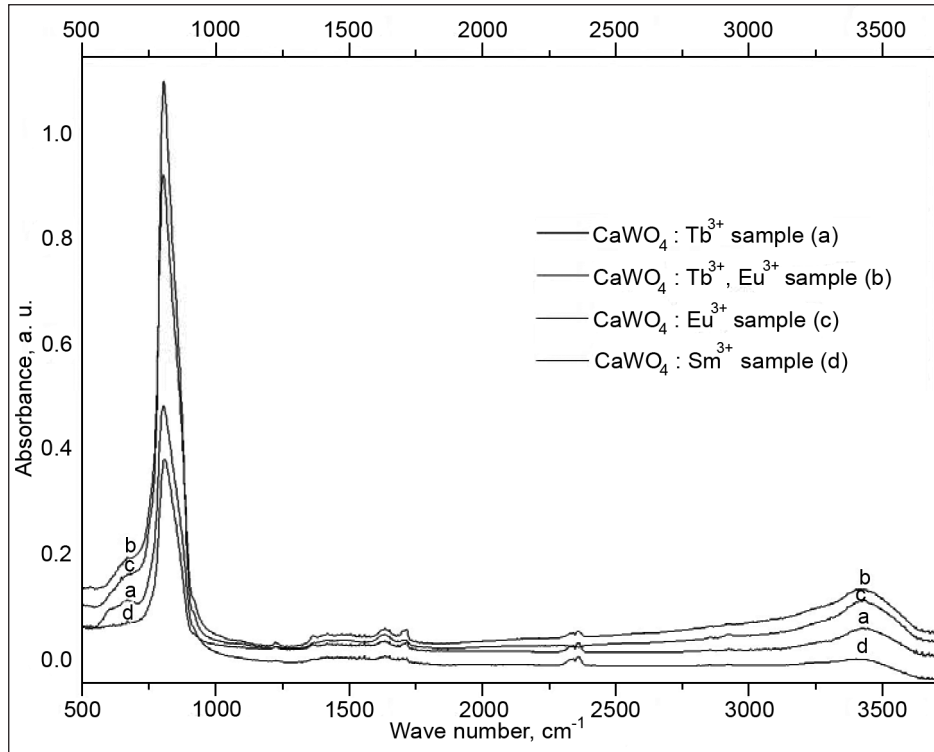


Fig. 2. IR absorption spectra of RE³⁺-ion doped CaWO₄ samples

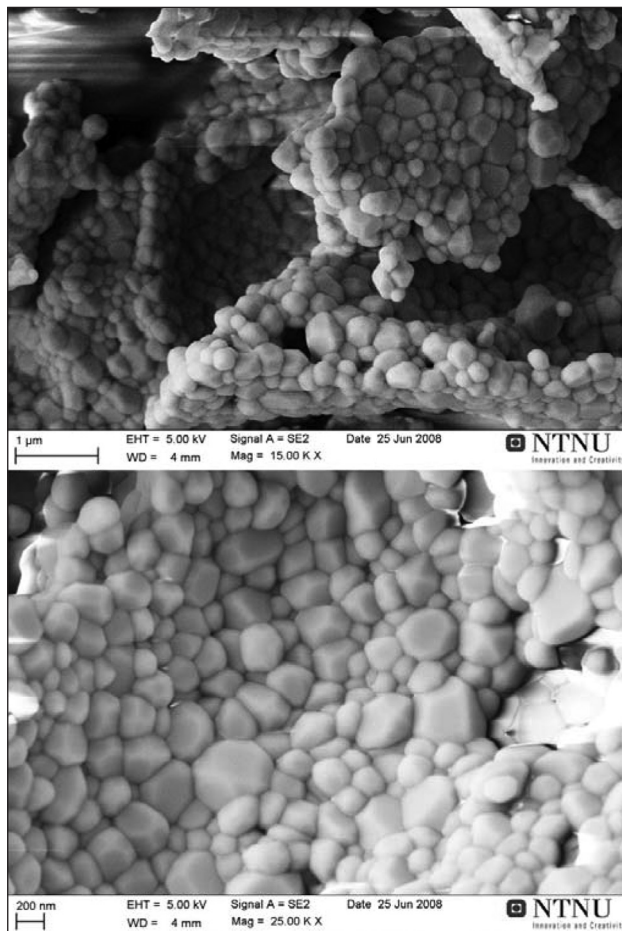


Fig. 3. Representative SEM images of Tb³⁺-ion doped CaWO₄ obtained at different magnifications

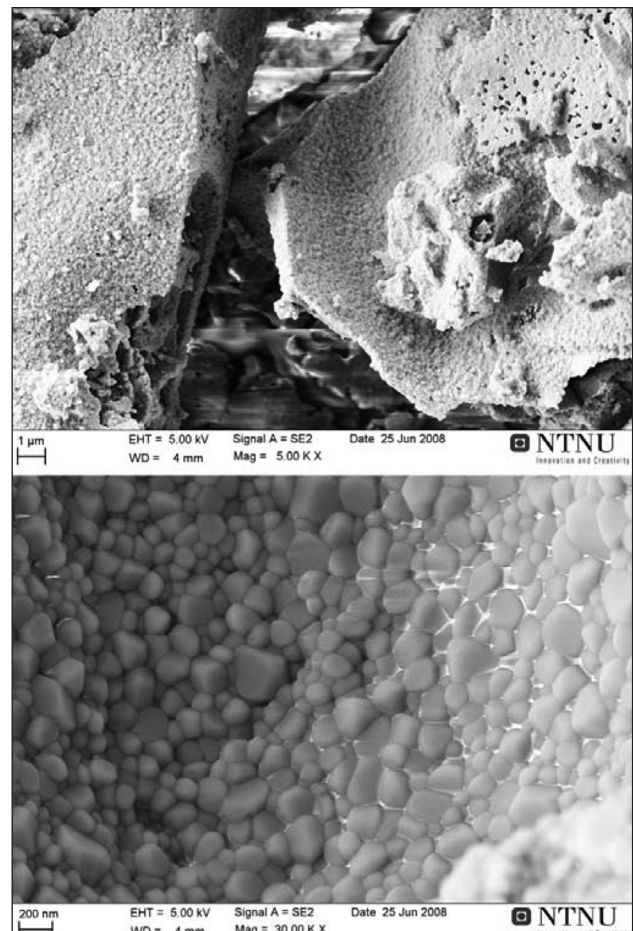


Fig. 4. Representative SEM images of Tb³⁺- and Eu³⁺-ion doped CaWO₄ obtained at different magnifications

precursor gels at 800 °C produces a fully crystalline CaWO_4 phase. The most intensive lines are: (112), 100% (at $2\theta \sim 28.5^\circ$); (101), $\sim 48\text{--}51\%$ (at around $2\theta \sim 18.0^\circ$); (204), $\sim 29\text{--}30\%$ (at around $2\theta \sim 47.3^\circ$). This observation is in good agreement with previously reported results obtained for the CaWO_4 phase [19]. Thus, the XRD data confirm that preparing different CaWO_4 :RE phosphores in the sol–gel process using tartaric acid as a complexing agent, the single polycrystalline calcium tungstate phase was synthesized at 800 °C. The results have led to the conclusion that the proposed sol–gel synthesis route is a very suitable method of preparing a single CaWO_4 phase homogeneously doped with different rare-earth metal ions.

IR absorption spectra were consistent with the results of XRD measurements, evidencing the crystallization process. The IR absorption spectra of CaWO_4 :RE samples synthesized by the nitrate–tartrate sol–gel method are shown in Fig. 2. The IR spectra of the CaWO_4 :RE samples calcined at 800 °C contain broad and intense bands peaking at $850\text{--}750\text{ cm}^{-1}$, which can be assigned to the characteristic vibrations of WO_4^{2-} in scheelite [20, 21]. Moreover, the IR spectra of rare-earth-element-doped calcium tungstate samples calcined at

800 °C did not show any bands attributable to carbonates or adsorbed water. The line broadening due to the local distortion of WO_4^{2-} group in powders [22] is also visible.

The textural properties of CaWO_4 :RE powder obtained at 800 °C were investigated by SEM. The typical morphological photographs of CaWO_4 :RE samples synthesized by the nitrate–tartrate sol–gel route are shown in Figs. 3–6. As is clearly seen in Figs. 3, 4 and 5, the Tb^{3+} - and Eu^{3+} -doped CaWO_4 solids are composed of plate-like and spherical grains. The SEM images at higher magnifications also reveal the obtained individual particles to be nanocrystals with an average particle size of less than 250 nm. It is important to note that Tb^{3+} -doped CaWO_4 particles are larger than those doped with Eu^{3+} . Moreover, CaWO_4 :Sm crystals have a different structure. As is seen in Fig. 6, the crystals are porous and contain no plate-like crystals which were observed in samples doped with Tb and Eu. Nevertheless, one can see in the pictures with a higher magnification that individual particles have a rather spherical shape. Also, it has been shown in previous cases that the obtained crystals are formed with a very well pronounced agglomeration, indicating a good conductivity among the grains. The SEM results evidently show that the morphological

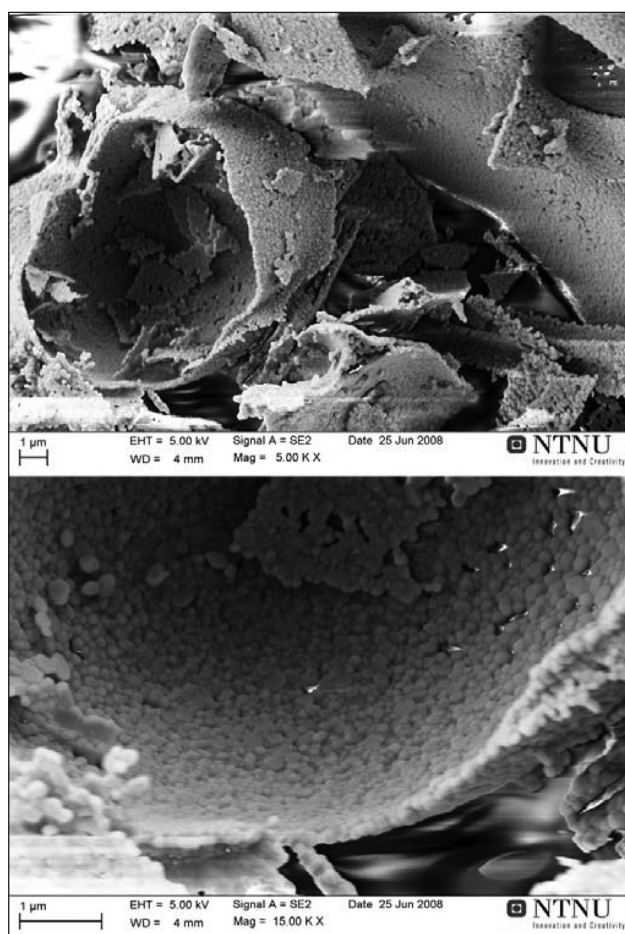


Fig. 5. Representative SEM images of Eu^{3+} -ion doped CaWO_4 obtained at different magnifications

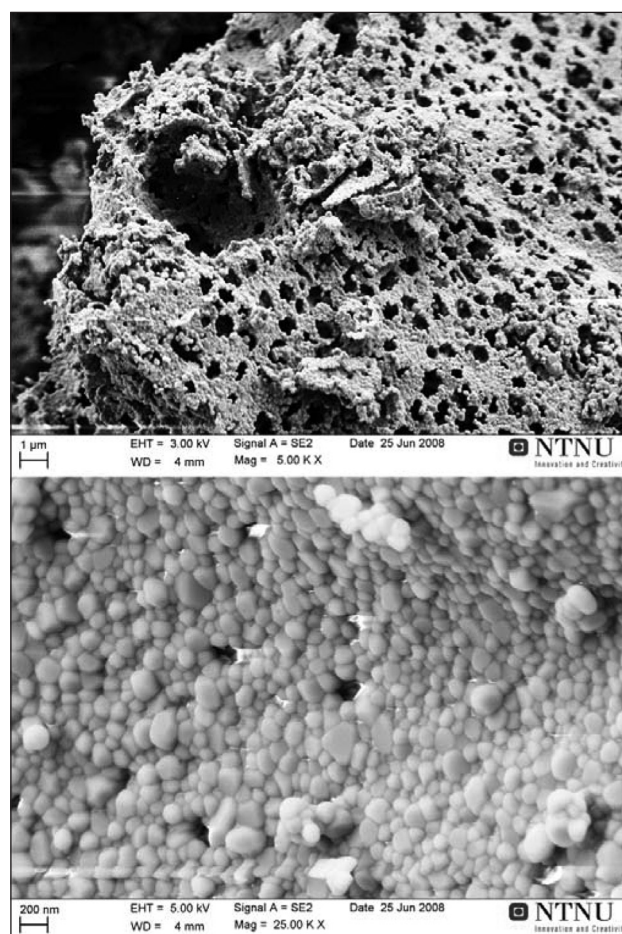


Fig. 6. Representative SEM images of Sm^{3+} -ion doped CaWO_4 products obtained at different magnifications

features of different lanthanide-activated calcium tungstates strongly depend on the nature of the doping metal. A particular strong effect on material structure was observed in the CaWO₄ sample doped with Sm³⁺. As is seen in Fig. 6, the size of the obtained crystals varies from 200 nm down to less than 100 nm. It is obvious that Sm³⁺-doped CaWO₄ contains smaller particles (~150 nm) than CaWO₄: Tb and CaWO₄: Eu. The largest particles are formed in CaWO₄: Tb where the average grain diameter was 250–300 nm. Moreover, agglomeration was more pronounced in CaWO₄: Tb, Eu than in CaWO₄: Sm.

The luminescence properties of CaWO₄ ceramics doped with different rare-earth metals synthesized using nitrate–tartrate sol–gel technique were also investigated. The emission spectra of CaWO₄: Tb, CaWO₄: Tb, Eu, CaWO₄: Eu and CaWO₄: Sm phosphores excited at the wavelengths of 280, 360 and 460 nm are presented in Figs. 7, 8, and 9, respectively. The most intensive emission was observed in the CaWO₄: Eu sample. Co-doping with Tb resulted in a very strong quenching of the emission. Only under excitation at 280 nm, the luminescence of CaWO₄: Tb, Eu was of similar though by a factor of ~10 lower intensity than that of CaWO₄: Eu. Note that terbium ions showed no significant emission either in CaWO₄: Tb, Eu or in CaWO₄: Tb at all the excitation wavelengths used. A broad band peaked at ~720 nm was observed in all samples under study; probably, it originated from the host material. The samples doped with Sm showed an emission typical of samarium ions. The strongest CaWO₄: Sm emission was observed under excitation at 460 nm, but emission was hardly observable at 280 nm.

CONCLUSIONS

CaWO₄: RE (RE = Tb³⁺, Eu³⁺, and Sm³⁺) were prepared by the aqueous sol–gel method using tartaric acid as a complexing agent. The X-ray diffraction data revealed that a single CaWO₄ crystalline phase was obtained in all samples with different doping. IR absorption spectra confirmed the existence of characteristic vibrations of M–O and WO₄²⁻ groups. The textural properties of CaWO₄: RE powder obtained at 800 °C were studied by SEM analysis. The SEM pictures of synthesized ceramics clearly evidenced formation of nanocrystals with an average particle size of less than

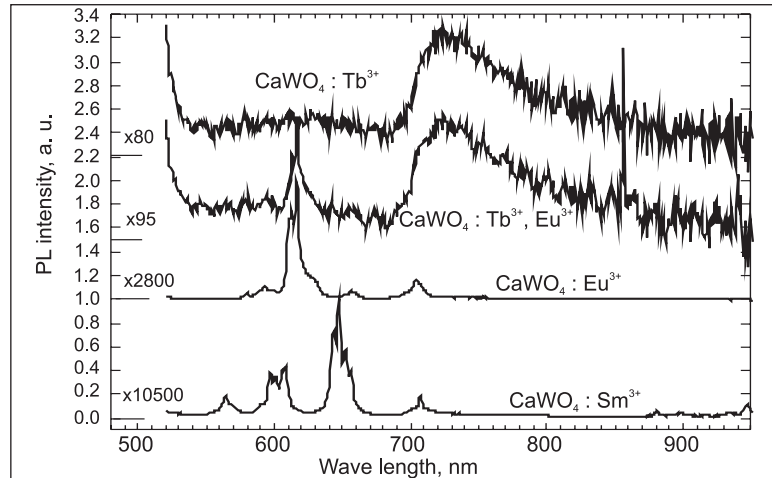


Fig. 7. Normalized photoluminescence spectra of RE³⁺-doped CaWO₄ phosphors prepared by sol–gel method under excitation at $\lambda_{\text{ex}} = 460$ nm. Spectra are normalized and vertically shifted for clarity; intensity factors are indicated

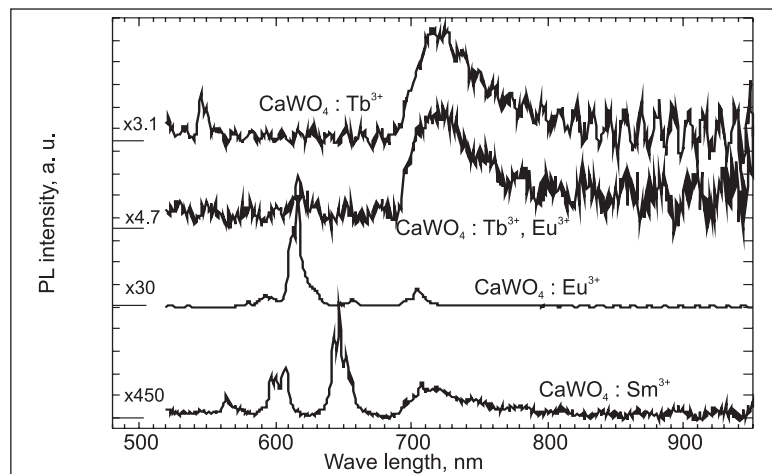


Fig. 8. Normalized photoluminescence spectra of RE³⁺-doped CaWO₄ phosphors prepared by sol–gel method under excitation at $\lambda_{\text{ex}} = 360$ nm. Spectra are normalized and vertically shifted for clarity; intensity factors are indicated

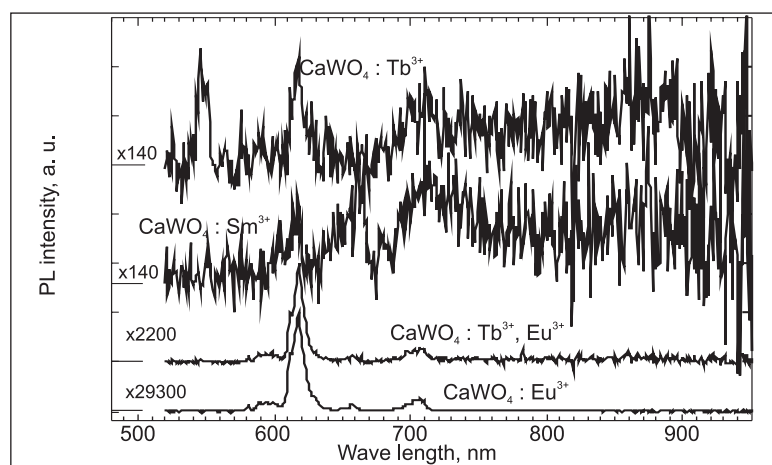


Fig. 9. Normalized photoluminescence spectra of RE³⁺-doped CaWO₄ phosphors prepared by sol–gel method under excitation at $\lambda_{\text{ex}} = 280$ nm. Spectra are normalized and vertically shifted for clarity; intensity factors are indicated

250 nm. Photoluminescence study under excitation at 280, 360, and 460 nm showed that CaWO_4 :Eu compound emission was by a factor of 10 to 100 more intensive than that of other CaWO_4 :RE samples. The results demonstrate that the aqueous sol-gel method could be successfully used for the preparation of lanthanide-doped CaWO_4 for applications as phosphor materials.

Received 8 May 2009

Accepted 19 May 2009

References

1. S. L. Porto, E. Longo, P. S. Pizani, L. G. P. Lima, J. M. Ferreira, L. E. B. Soledada, J. W. M. Espinoza, M. R. Cassia-Santos, M. A. M. A. Maurera, C. A. Paskocimas, I. M. G. Santos, A. G. Souza, *J. Solid State Chem.*, **181**, 1876 (2008).
2. S. Shi, J. Gao, J. Zhou, *Opt. Mater.*, **30**, 1616 (2008).
3. R. Manalert, M. N. Rahaman, *J. Mater. Sci.*, **31**, 3453 (1996).
4. E. Comini, A. Toncelli, M. Tonelli, E. Zannoni, E. Cavalli, A. Speghini, M. Bettinelli, *J. Opt. Soc. Am. B*, **14**, 1938 (1997).
5. J. T. Vega-Duran, O. Barbosa-Garcia, L. A. Diaz-Torres, M. A. Meneses-Nava, D. S. Sumida, *Appl. Phys. Lett.*, **76**, 2032 (2000).
6. W. Streck, A. Bednarkiewicz, P. J. Dere'n, *J. Lumin.*, **92**, 229 (2001).
7. A. Nosenko, L. Kostyk, L. Koslovs'ka, *J. Lumin.*, **90**, 49 (2000).
8. Y. R. Do, Y. D. Huh, *J. Electrochem. Soc.*, **147**, 4385 (2000).
9. F. Shi, J. Meng, Y. Ren, Q. Su, *J. Phys. Chem. Solids*, **59**, 105 (1998).
10. N. V. Kuleshov, A. A. Lagatsky, A. V. Podlipensky, V. P. Mikhailov, G. Huber, *Opt. Lett.*, **22**, 1317 (1997).
11. Y. Urata, T. Fukuda, H. Ito, S. Wada, *Jpn. J. Appl. Phys.*, **40**, 6453 (2001).
12. Y. Chen, X. Lin, Z. Luo, Y. Huang, *Chem. Phys. Lett.*, **381**, 598 (2003).
13. Q. Wei, D. Chen, *Opt. Laser Technol.* (2009), doi:10.1016/j.optlastech.2008.12.003.
14. V. N. Kolobanov, I. A. Kamenskikh, V. V. Mikhailin, I. N. Shpinkov, D. A. Spassky, B. I. Zadneprovsky, L. I. Potkin, G. Zimmerer, *Nucl. Instrum. Methods A*, **486**, 496 (2002).
15. V. Nagirnyi, E. Feldbach, L. Jonsson, M. Kirm, A. Lushchik, C. Lushchik, L. L. Nagornaya, V. D. Ryzhikov, F. Savikhiu, G. Svensson, I. A. Tupitsina, *Radiat. Meas.*, **29**, 247 (1998).
16. G. R. Choppin, D. R. Peterman, *Coord. Chem. Rev.*, **174**, 283 (1998).
17. S. Lis, M. Elbanowski, B. Makowska, Z. Hnatejko, *J. Photochem. Photobiol. A*, **150**, 233 (2002).
18. A. Patra, D. Kundu, D. Ganguli, *Mater. Lett.*, **32**, 43 (1997).
19. S. J. Chen, J. Li, X. T. Chen, J. M. Hong, Z. Xue, X. Z. You, *J. Cryst. Growth*, **253**, 361 (2003).
20. L. J. Burcham, I. E. Wachs, *Spectrochim. Acta A*, **54**, 1355 (1998).
21. R. R. Khanna, E. R. Lippincott, *Spectrochim. Acta A*, **24**, 905 (1968).
22. P. Mogilevsky, T. A. Parthasarathy, M. D. Petry, *Acta Materialia*, **52**, 5529 (2004).

Artūras Žalga, Rokas Sažinas, Edita Garškaitė, Aivaras Kareiva, Tomas Bareika, Gintautas Tamulaitis, Remigijus Juškėnas, Rimantas Ramanauskas

CaWO_4 FOSFORŲ, AKTYVUOTŲ RE^{3+} JONAIŠ, SINTEZĖ ZOLIŲ-GELIŲ METODU

Santrauka

Zolių-gelių metodu, pradinėmis medžiagomis naudojant WO_3 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Tb_4O_7 , Eu_2O_3 ir Sm_2O_3 , buvo susintetinti nanokristaliniai lantanoidų jonais aktyvuoti kalcio volframato (CaWO_4) fosforai. Susintetinti RE^{3+} : CaWO_4 pavyzdžiai buvo tirti infraraudonoji spektrometrija (IR), Rentgeno spindulių difrakcija (XRD), skenuojančia elektronine mikroskopija (SEM) bei fotoluminescencine analize (PL). Rezultatai parodė, kad gelius iškaitinus 800 °C temperatūroje, susiformavo vienfaziai CaWO_4 fosforai, kurie gali būti sužadinti 280, 360 ir 460 nm spinduliuote ir gali emituoti šviesą 620 nm spektro srityje.