

Terbium doped and europium doped NaAlSiO₄ nano glass-ceramics for LED application

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Terbium doped and europium doped homogeneous glasses from the system Na₂O-Al₂O₃-SiO₂-NaBO₂ are prepared. Glass-ceramics are obtained after thermal treatment of the parent glass at different temperatures and time. The crystallizing phases, the degree of crystallinity and the particle size are determined. The main crystallizing phase after thermal treatment is NaAlSiO₄. X-ray analyses show the presence of Na₂SiO₃ as the second phase. The crystallinity degree after 24h thermal treatment at 650°C of the glass-ceramic samples is about 90%. The particle size for NaAlSiO₄ is between 50 and 60 nm, and for Na₂SiO₃ - between 30 and 70 nm. Emission and excitation spectra of the glass-ceramics show the characteristic peaks of Tb³⁺ and Eu³⁺. The main emission peak of Tb³⁺ is ⁵D₄ → ⁷F₅ transition at 549 nm, corresponding to green color. The Tb³⁺ excitation spectrum shows the strongest peak located at 379 nm. The main emission peak of Eu³⁺ is ⁵D₀ → ⁷F₂ transition at 612 nm, corresponding to orange-red color. The Eu³⁺ excitation spectrum shows the strongest peak located at 393 nm.

Keywords: Silicate phosphor, Nano glass-ceramic, Rare-earth ions, X-ray, Photoluminescence

INTRODUCTION

Light emitting diodes (LED) are of special interest as they are environmental friendly and efficient energy saving devices [1, 2]. The commercial white LEDs (WLEDs) can be realized by combining a blue chip with yellow phosphor or by combining of blue, green and red (RGB) emitting tricolor multiphased phosphors [1, 3]. Therefore, it is important to investigate novel blue, red and green phosphors which show high emission intensities.

The luminescence behavior of the rare earth activated phosphors depends strongly on the composition of the host, concentration of the activator and methods of preparation [3]. Silicates are one of the most suitable materials because of their high chemical and mechanical stability and various crystal structures [2]. In addition, silicate glasses and glass-ceramics doped by rare earth ions are among the most commonly used materials for optical fibers, wave guides for opto-electronic communication and color display devices. Many investigations are published on Eu²⁺ and Mn²⁺ doped (Ba,Sr)3MgSi₂O₈ [4], Ce³⁺ and Tb³⁺ doped BaLu₂Si₃O₁₀ [5], Eu²⁺ doped Ba₂Zn₃Si₃O₁₁ [6], Ce³⁺ and Eu²⁺ doped Ca₃Si₂O₇ [7], Ce³⁺ and Mn²⁺ doped Ca₃Sc₂Si₃O₁₂ [8],

Li₂SiO₃ doped by Er³⁺, Eu³⁺, Dy³⁺, Sm³⁺, Tb³⁺, Ce³⁺ [9, 10], Eu²⁺ doped NaAlSiO₄ [11], Ce³⁺ and Mn²⁺ doped NaAlSiO₄ [12], Fe³⁺ doped NaAlSiO₄ [13], Eu²⁺ doped NaAlSiO₄ [14], Tb³⁺ doped NaAlSiO₄ [15], Dy³⁺ doped NaAlSiO₄ [16]. These compounds are synthesized by conventional solid state method or by sol-gel method. Compared with these phosphors and glasses, rare earth doped glass-ceramics are a good alternative because of the low cost preparation process, simple manufacturing procedure, free from halo effect. Mechanical, thermal, electrical and optical properties of the material could be improved by controlled heat treatment of the parent glass [17-19].

NaAlSiO₄ compound is with nepheline like structure.

The crystal structure of this compound is hexagonal with space group P63. It consists of AlO₄ and SiO₄ tetrahedra, connected with oxygen bridges. Charge compensation is achieved by incorporation of sodium cations in the cavities of the structure [20, 21]. At room temperature the nepheline compound also exists in different polymorphic modifications, depending on the method of preparation [22, 23]. These modifications transform themselves to hexagonal at 160 – 200°C [24].

NaAlSiO₄ glass-ceramics are investigated for optical and telecommunication systems

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applications, [19, 25], for medical applications [26, 27], for ceramic hot plates and microwave ovens [28]. The structure of NaAlSiO₄ allows doping by Rare Earth ions.

Tb³⁺ and Eu³⁺ doped phosphor materials have a strong excitation band in the near UV region. Tb³⁺ ion shows green emission due to ⁵D₄→⁷F₅ transition. The increase of Tb³⁺ concentration leads to decrease of emission intensity from ⁵D₃, which is due to cross relaxation between ⁵D₃→⁷F₁ and ⁷F₁→⁵D₄. Eu³⁺ ion shows orange-red emission corresponding to ⁵D₀→⁷F₁ or ⁵D₀→⁷F₂ transitions [3, 10, 15].

In this paper we report our efforts to obtain Tb³⁺ and Eu³⁺ doped NaAlSiO₄ nano glass-ceramics for LED applications. To our knowledge this kind of investigations are not published to this moment.

EXPERIMENTAL

Na₂CO₃ (p.a.), Al₂O₃ (p.a.), SiO₂ (p.a.), H₃BO₃ (p.a.), Tb₄O₇ (p.a.) and Eu₂O₃ (p.a.) were used as raw materials. Glass synthesis were carried out in a resistive furnace with Kantal heating wire permitted maximum working temperature of 1200 °C and in a chamber furnace with MoSi₂ heating elements permitted maximum working temperature of 1550 °C. The temperature was controlled with Pt/Pt–10%Rh thermocouple and Eurotherm controller. Glasses were melted in platinum crucibles. First the mixture was heated at 700 °C for decomposition of the sodium carbonate and boric acid. Then the melt was heated at 1400 °C during 4h for homogenization and obtained glass were cooled to the room temperature by quick removing from the furnace. Finally the glasses were thermally treated for establishing of the crystallizing phases. The structural characterization was carried out by powder X-ray diffraction using a Bruker D8 Advance powder diffractometer with Cu Kα radiation and SolX detector. X-ray diffractograms were recorded at room temperature. Data were collected in the 2θ range from 10 to 80° with a step 0.04° and 1 s step–1 counting time. X-ray diffractograms were identified using the Diffractplus EVA program. The mean crystallite size were calculated from the integral breadth of all peaks using Scherrer equation and the TOPAS 3 program 3 – General profile and structure analysis software for powder diffraction data, 2005, Bruker AXS, Karlsruhe, Germany. The area of the amorphous phase was determined by using a straight line for description of the background and single line for fitting the

amorphous component. The emission and excitation spectra were measured on Horiba Fluorolog 3-22 TCS spectrophotometer equipped with a 450 W Xenon Lamp as the excitation source. All spectra were measured at room temperature.

RESULTS AND DISCUSSION

Our previous investigations show, that the glasses from the system Na₂O-Al₂O₃-SiO₂-B₂O₃ are suitable for preparation of the glass-ceramics containing NaAlSiO₄ phase. For these investigations NaAlSiO₄-NaBO₂ = 66:34 component ratio was chosen and the concentration of the dopants was 0.25, 0.33 and 0.5 at% for Tb³⁺ or 0.1 at% for Eu³⁺ related to NaAlSiO₄. The experiments show that the maximal terbium concentration is 0.5 at.% and the maximal europium concentration is 0.1 at.%, at which the homogeneous glasses can be prepared in the described conditions.

The glasses were thermally treated at 650°C during 2, 5 and 24 h for determination of the crystallizing phases, crystal part and mean particle size of the nano-crystals. These regimes were chosen on the base of our previous investigations. The result after thermal treatment at lower temperatures is a large glass part and small peaks of NaAlSiO₄. Thermal treatment of the glasses at 650°C more than 5h leads to crystallization of NaAlSiO₄ and Na₂SiO₃ in both terbium and europium doped glasses. XRD patterns of the terbium doped glass treated at 650°C during 24h is shown in Fig. 1.

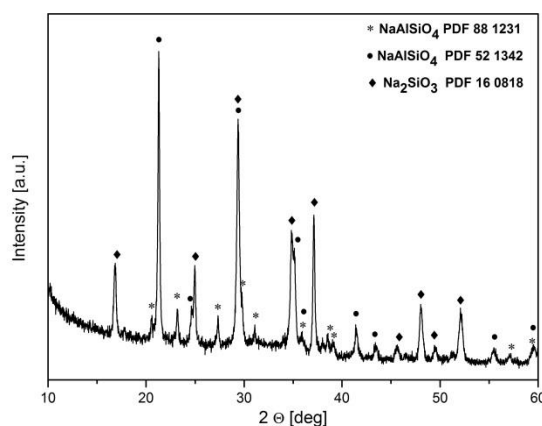


Fig. 1. XRD patterns of the terbium doped glass ceramic treated at 650°C during 24h.

Crystal part of the samples doped by 0.5 at.% Tb³⁺ or 0.1 at.% Eu³⁺ treated at 650°C with different duration and the ratio between two

crystallizing phases NaAlSiO₄ and Na₂SiO₃ are presented in Table 1. As can be seen from the table, terbium makes the crystallization process more difficult in thermal treatment during 5h. So the crystallinity degree of terbium-doped glass-ceramic is 54%, while the degree of crystallinity of europium-doped glass-ceramic is 78%. The crystallinity degree after 24h thermal treatment is about 90%. XRD patterns of the samples treated at 650°C for 5 and 24h, presented in Fig. 2, show the same tendency. The intensity of the peaks is in a good collation with the crystallinity degree.

Table 1. Crystal part of the samples doped by 0.5 at.% Tb³⁺ and 0.1 at.% Eu³⁺ treated at 650°C with different duration [%] and ratio between two crystallizing phases NaAlSiO₄ and Na₂SiO₃.

Sample	Tb:NaAlSiO ₄	Eu:NaAlSiO ₄
Time[h]		
2	glass	
5	54%	78%
	68:32	69:31
24	88%	90%
	71:29	70:30

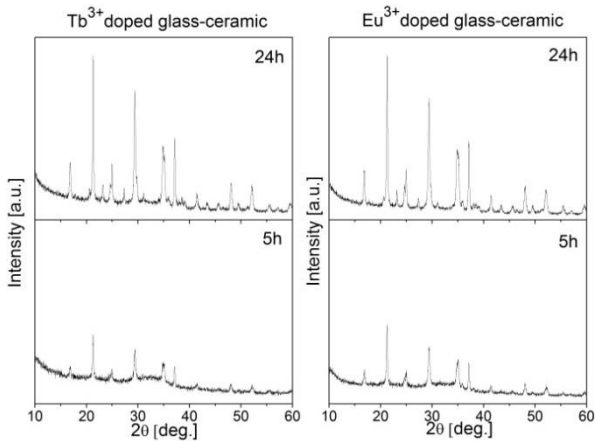


Fig. 2. XRD patterns of the samples doped by 0.5 at.% Tb and 0.1 at.% Eu treated at 650°C during 5 and 24h.

The ratio between the two crystallizing phases NaAlSiO₄ and Na₂SiO₃ is 70:30 and does not depend on the dopants and thermal treatment time. The mean particle size for NaAlSiO₄ nanocrystals is between 50 and 60 nm and weak depend on the dopants and thermal treatment time. The particle size of Na₂SiO₃ nanocrystals is between 30 and 70 nm.

Emission and excitation spectra of 0.5 at.% Tb³⁺ doped sample and 0.1 at.% Eu doped sample treated at 650°C during 24h are presented in Fig. 3. The Tb³⁺:NaAlSiO₄ glass-ceramic excitation spectrum covers the range from 300 to 500 nm. The sample shows characteristic transitions of

Tb³⁺: ⁷F₆→⁵H₇ transition for 317 nm, ⁷F₆→⁵D₂ transition for 350 nm, ⁷F₆→⁵L₁₀ transition for 357 nm, ⁷F₆→⁵D₃ transition for 379 nm, and the ⁷F₆→⁵D₄ transition for 482 nm. These lines are attributed to the f-f transitions of Tb³⁺. The strongest peak is located at 379 nm corresponding to the ⁷F₆→⁵D₃ transition.

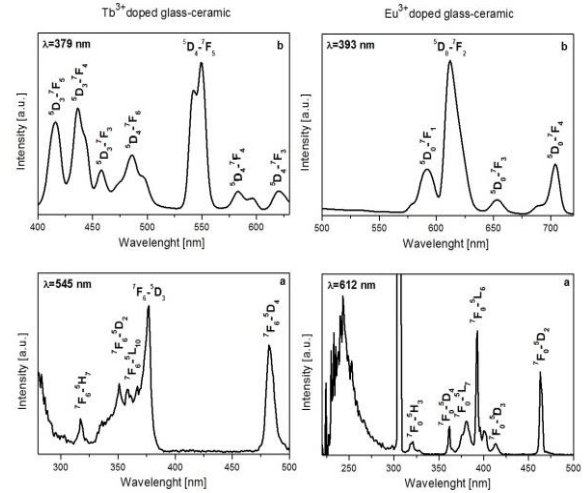


Fig. 3. Excitation (a) and emission (b) spectra of the 0.5 at.% Tb doped glass-ceramic sample and 0.1 at.% Eu doped glass-ceramic sample treated at 650°C during 24h. CIE 1931 coordinates for Tb³⁺ doped sample x=0.23, y=0.27. CIE 1931 coordinates for Eu³⁺ doped sample x=0.45, y=0.29.

The main emission peak of Tb³⁺:NaAlSiO₄ glass-ceramic is ⁵D₄→⁷F₅ transitions at 549 nm, corresponding to green color. Other transitions from ⁵D₃→⁷F₅, ⁵D₃→⁷F₄, ⁵D₄→⁷F₆, ⁵D₄→⁷F₄ and ⁵D₄→⁷F₃ are located at 415, 436, 458, 485, 583 and 620 nm [3, 29].

The Eu³⁺:NaAlSiO₄ glass-ceramic excitation spectrum covers the range from 300 to 500 nm. The sample shows characteristic transitions of Eu³⁺: ⁷F₀→⁵H₃ transition for 320 nm, ⁷F₀→⁵D₄ transition for 361 nm, ⁷F₀→⁵L₇ transition for 380 nm, ⁷F₀→⁵L₆ transition for 393 nm, ⁷F₀→⁵D₃ transition for 413 nm, and ⁷F₀→⁵D₂ transition for 463 nm. These lines are attributed to the f-f transitions of Eu³⁺. The strongest peak is located at 393 nm corresponding to the ⁷F₀→⁵L₆ transition. The band around 250 nm is due to the charge transfer Eu³⁺-O²⁻.

The main emission peak of Eu³⁺:NaAlSiO₄ glass-ceramic is ⁵D₀→⁷F₂ transitions at 612 nm, corresponding to orange-red color. Other transitions from ⁵D₀→⁷F₁, ⁵D₀→⁷F₃ and ⁵D₀→⁷F₄ are located at 592, 653 and 704 nm. The red emission at 612 nm is an electric dipole transition

and displays the highest intensity. The orange emission at 592 nm is allowed magnetic dipole transition. The second emission intensity is lower, which indicates that Eu³⁺ ions occupy sites without an inversion center [3, 30, 31].

Comparison of the samples with different concentrations of terbium ion is shown in Fig. 4. It is seen that the Tb³⁺ emission is the most intense at a concentration of 0.5 at% in the investigated concentration range.

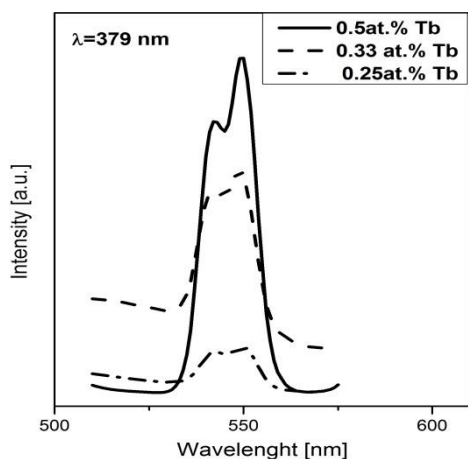


Fig. 4. The emission spectra of samples with different terbium ion concentration.

Comparison of the spectrum of Tb³⁺:NaAlSiO₄ glass-ceramic with those of the sol-gel prepared Tb³⁺:NaAlSiO₄ powder [15] show difference in the range 400-530 nm. The peaks in the first spectrum are more intensive and clearer. This may be due to the additional emission from some part of the glass and Na₂SiO₃ as the second phase. The spectrum of Eu³⁺:NaAlSiO₄ glass-ceramic is very similar to the spectrum published for Eu³⁺ doped NaAlSiO₄-NaY₉Si₆O₂₆ glass-ceramic [31].

CONCLUSION

Terbium doped and europium doped homogeneous glasses from the system Na₂O-Al₂O₃-SiO₂-NaBO₂ are prepared with the highest concentration of the dopants 0.5 at% for Tb³⁺ and 0.1 mol% for Eu³⁺. Glass-ceramics are obtained after thermal treatment of the parent glass at different treatment time. The main crystallizing phase after thermal treatment at 650 °C with different duration is NaAlSiO₄ and some presence of Na₂SiO₃ as a second phase is detected. The ratio between these two phases is 70:30. The crystallinity degree of the glass-ceramic samples could reach up to 90%. The particle size for the two crystallizing phases is between 30 and 70 nm.

Emission and excitation spectra of the glass-ceramics show the characteristic peaks of Tb³⁺ and Eu³⁺.

The obtained results show that as prepared terbium doped NaAlSiO₄ glass-ceramics could be used as a green phosphor. Europium doped NaAlSiO₄ glass-ceramics could be used as an orange-red phosphor. It would be interesting to find a suitable terbium and europium concentration into the glass-ceramics, giving the mix between these two colors.

REFERENCES

1. C. Lin, R. Liu, *J. Phys. Chem. Lett.*, **2**, 1268 (2011).
2. M. Shur, A. Zukauskas, *Proc. IEEE*, **93**, 1691 (2005).
3. W. Yen, S. Shionoya, H. Yamamoto, *Phosphor Handbook*, CRC Press, Boca Raton, 1998.
4. Q. Lu, J. Li, D. Wang, *Curr. Appl. Phys.*, **13**, 1506 (2013).
5. K. Li, S. Liang, H. Lian, M. Shang, B. Xing, J. Lin, *J. Mat. Chem. C*, (2016) (in press).
6. D. Wei, Y. Huang, S. Kim, Y. Yu, H. Seo, *Mater. Lett.*, **99**, 122 (2013).
7. L. Wenzhen, G. Ning, J. Yongchao, Z. Qi, Y. Hongpeng, *Opt. Mater.*, **35**, 1013 (2013).
8. Y. Liu, X. Zhang, Z. Hao, Y. Luo, X. Wang, L. Ma, J. Zhang, *J. Lumin.*, **133**, 21 (2013).
9. I. Sabikoglu, M. Ayvacıklı, A. Bergeron, A. Ege, N. Can, *J. Lumin.*, **132**, 1597 (2012).
10. Y. Naik, M. Mohapatra, N. Dahale, T. Seshagiri, V. Natarajan, S. Godbole, *J. Lumin.*, **129**, 1225 (2009).
11. D. Jo, Y. Luo, K. Senthil, K. Toda, B. Kim, T. Masaki, D. Yoon, *Opt. Mater.*, **34**, 696 (2012).
12. J. Zhou, T. Wang, X. Yu, D. Zhou, J. i Qiu, *Mat. Res. Bull.*, **73**, 1 (2016).
13. M. Nayak, T.R.N. Kutty, *Mater. Chem. Phys.*, **57**, 138 (1998).
14. G. Yuzhu, Y. Xibin, L. Jie, Y. Xuyong, *J. Rare Earth*, **28**, 34 (2010).
15. J. Dhoble, B. Kore, A. Yerpude, R. Kohale, P. Yawalkar, N. Dhoble, *Optik*, **126**, 1527 (2015).
16. A. Kumar, S. Dhoble, D. Peshwe, J. Bhatt, *J. Alloy. Compd.*, **609**, 100 (2014).
17. P. Babu, K. Jang, S. Rao, L. Shi, C. Jayashankar, V. Lavin, H. Seo, *Opt. Express*, **19**, 1836 (2011).
18. R. Krsmanovic, S. Bals, G. Bertoni, G. Tendeloo, *Opt. Mater.*, **30**, 1183 (2008).
19. D. Chen, W. Xiang, X. Liang, J. Zhong, H. Yu, M. Ding, H. Lu, Z. Ji, *J. Eur. Ceram. Soc.*, **35**, 859 (2015).
20. T. Hahn, M.J. Buerger, *Z. Kristallographie*, **106**, 308 (1955).
21. K. Tait, E. Sokolova, F. C. Hawthorne, *Can. Mineral.*, **41**, 61 (2003).

22. C. Henderson, J. Roux, *Contrib. Mineral. Petr.*, **61**, 279 (1977).
23. C. Henderson, A. Thompson, *Am. Mineral.*, **65**, 970 (1980).
24. H. Schneider, O. Flörke, R. Stoeck, *Z. Kristallographie*, **209**, 113 (1994).
25. M. Hirose, T. Kobayashi, K. Maeda, *Reports Res. Lab. Asahi Glass Co., Ltd.*, **55** (2005).
26. E. Hamzawya, E. El-Meliqy, *Mat. Chem. Phys.*, **112**, 432 (2008).
27. M. Wang, N. Wu, M. Hon, *Mat. Chem. Phys.*, **37**, 370 (1994).
28. J. Mac Dowell, *J. Am. Ceram. Soc.*, **58**, 258 (1975).
29. G. Blaase, B. C. Grabmeier, *Luminescent materials*, Springer (1994).
30. S. Lu, J. Zhang, *J. Lumin.*, **122**, 500 (2007).
31. R. Bagga, V. Achanta, A. Goel, J. Ferreira, N. P. Singh, D. Singh, V. Contini, M. Falconieri, G. Sharma, *Opt. Mater.*, **36**, 198 (2013).

ДОТИРАНА С ТЕРБИЙ И ЕВРОПИЙ НАНОРАЗМЕРНА СЪКЛОКЕРАМИКА СЪДЪРЖАЩА NaAlSiO₄ ЗА ПРИЛОЖЕНИЕ КАТО ЛУМИНЕСЦЕНТЕН МАТЕРИАЛ

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(Резюме)

Синтезирани са дотирани с тербий и европий хомогенни стъкла от системата Na₂O-Al₂O₃-SiO₂-NaBO₂. Стъклокерамиката е получена след термично третиране на тези стъкла при различни температури с различна продължителност. Определени са кристализиращите фази, степента на кристалност и размера на частиците в стъклокерамиката. Основната кристализираща фаза след термично третиране е NaAlSiO₄. Рентгеновите анализи показват наличието на Na₂SiO₃ като втора кристализираща фаза. Степента на кристалност на стъклокерамиката след термично третиране при 650°C в продължение на 24 часа е около 90%. Размерът на частиците на NaAlSiO₄ е между 50 и 60 nm, а на Na₂SiO₃ – между 30 и 70 nm. Спектрите на емисия и възбуждане на стъклокерамиката показват характерните за йоните Tb³⁺ и Eu³⁺ пикове. Основният емисионен пик за Tb³⁺ се дължи на прехода ⁵D₄ → ⁷F₅ и е локализиран при 549 nm, отговарящ на зелен цвят. Спектърът на възбуждане показва най-интензивен пик при 379 nm. Основният емисионен пик за Eu³⁺ се дължи на прехода ⁵D₀ → ⁷F₂ и е локализиран при 612 nm, отговарящ на оранжево-червен цвят. Спектърът на възбуждане показва най-интензивен пик при 393 nm.