

Preparation of chromium doped glass-ceramics containing NaAlSiO₄ and Na₃B₃O₆ phases

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Pure and chromium doped homogeneous glasses from the systems Na₂O-Al₂O₃-SiO₂ and Na₂O-Al₂O₃-SiO₂-B₂O₃ are prepared. Transparent 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. Absorption and emission spectra are presented for the glass-ceramic sample with crystallizing phases NaAlSiO₄ and Na₃B₃O₆. The spectra show co-existing emission of the Cr³⁺ and Cr⁴⁺ ions and are discussed in the terms of Cr³⁺ and Cr⁴⁺ ions.

Keywords: NaAlSiO₄, chromium doped glass-ceramics, X-ray diffraction, absorption and emission spectra

INTRODUCTION

Tunable lasers are widely used in medicine and engineering. They allow customizing the laser radiation wavelength depending on the specific application. Especially attractive are lasers operating in the near infrared range (1.1 - 1.6 μm), important for optical communications, remote sensing and biomedical applications (as called eye-safe wavelength range). Suitable active ion emitting in this range is Cr⁴⁺ being in tetrahedral position. Therefore, a proper for Cr⁴⁺ doped laser matrix is particularly important. Obtaining of single crystals from many silicates, germinates and garnets is connected with different technological problems [1-10]. In recent years more researchers are interested in obtaining of glass-ceramics substituting the relevant single crystals. Chromium doped glass-ceramics obtaining is published for different compounds - Cr⁴⁺:Mg₂SiO₄ [11], Cr⁴⁺:Ca₂GeO₄ [12], Cr⁴⁺:LiGaSiO₄ [13, 14], Cr⁴⁺:Li₂ZnSiO₄ [15], Cr⁴⁺:Li₄SiO₄ [16], Cr⁴⁺:YAG [17]. Most of these glass-ceramics are connected with too high glass melt and homogenization temperatures.

In this paper the investigation of Cr⁴⁺ doped glass-ceramics from the systems Na₂O-Al₂O₃-SiO₂ and Na₂O-Al₂O₃-SiO₂-B₂O₃ glasses is reported. Crystallizing from these glasses compound NaAlSiO₄ is with nepheline like structure. The

crystal structure is hexagonal with space group P6₃. It consists of AlO₄ and SiO₄ tetrahedra, connected with oxygen bridges [18, 19]. Nepheline compound exists at room temperature also in different polymorphic modifications, depending on the method of preparation [20-22]. Non-doped nepheline glass-ceramics were investigated for optical and telecommunication systems applications [23], for medical applications [24, 25], for ceramic hot plates and microwave ovens [26].

The presence only of AlO₄ and SiO₄ tetrahedra in the nepheline structure is favorable for doping of the matrix with chromium ion in 4+ state of oxidation. 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.) and Cr₂O₃ (p.a.) was 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 using a Pt/Pt-10%Rh thermocouple connected to a Eurotherm controller. Glasses of the desired compositions were melted in platinum crucibles. First the mixture was heated at 700°C for decomposition of the carbonates and boric acid and then the powder was heated at the proper

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temperature for homogenization. As obtained glass were cooled to the room temperature by quick removing from the furnace. Some of the glasses were quenched by pouring onto a steel plate and pressing with another steel plate. The prepared glasses were thermally treated for phase nucleation into the glass. Structural characterization was carried out by powder X-ray diffraction (XRD) using a Bruker D8 Advance powder diffractometer with Cu K α radiation and SolX detector. X-ray diffractograms were recorded at room temperature. X-ray diffractograms were identified using the Diffractplus EVA program. The mean crystallite size was calculated from the integral breadth of all peaks (Pawley fit) 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 particle morphology were determined using a Transmission electron microscopy JEOL model JEM 200 CX accomplished with EM-ASID3D scanning attachment, working in secondary electrons regime. Specimens were covered with carbon-gold film. The particle size distribution was determined by the micrographs using Lince v2.4 – Linear Intercept program. The UV–Vis spectra were taken with a Thermo Evolution 300 UV-Vis Spectrophotometer equipped with a Praying Mantis device. The emission spectra were measured with 813.4 nm excitation by laser diode ATC-C1000-100-TMF-808-10. InGaAs ID-441-C was as detector in near infrared. The emissions from a black body specimen at determined temperature were utilized for standardization of the data. All spectra were established at room temperature.

RESULTS AND DISCUSSION

Two series of glasses were synthesized:

1. Glasses from the system Na₂O·Al₂O₃·2SiO₂-Na₂O·SiO₂ with different ratio between the two phases. The ratio is conforming to the phase diagram Na₂O-Al₂O₃-SiO₂ [27, 28]. The glasses are with eutectic composition between Na₂O·Al₂O₃·2SiO₂-Na₂O·SiO₂ at 915°C or on the isotherms at 768 and 900°C in the field of nepheline crystallization;

2. Glasses from the system NaAlSiO₄-NaBO₂. It was expected that NaBO₂ decrease the melting and homogenization temperature of the glass and by increasing of the viscosity to suppress the glass crystallization during its cooling.

The obtained glasses were thermally treated at different temperatures and with different duration. The content of the glasses, the homogenization temperatures, the homogenization time, the thermal treatment temperatures, the thermal treatment time and the crystallizing phases obtained after thermal treatment are listed in Table 1.

As can be seen from the table, for the glasses numbered from 1 to 4 higher temperature for homogenization is required, but the process time is shorter. In the opposite, the glasses containing B₂O₃ numbered from 5 to 7, homogenized at significant lower temperature (200°C lower). At this lower temperature the evaporation of B₂O₃ is absent. Of course, the homogenization time in this case is longer. In all investigated glasses under the described conditions of thermal treatment except the desired phase another phases are observed. In the glasses 1, 2 and 4 this phase is Na₂SiO₃ (Fig. 1). In the borate glasses the second phase depends on the content of the chromium oxide. In non-doped glass crystallizes NaBO₂ (Fig. 2a). In the glasses doped by 5 at.% Cr, a part of Cr₂O₃ crystallizes as a second phase (Fig. 2b). The quantity of the Cr₂O₃ decreases with increasing of the treatment time. In the glasses doped by 2 at.% Cr, Na₃B₃O₆ crystallizes as a second phase (Fig. 2c). We choose to investigate more detailed glasses with composition 7. This glass could be obtained at lower temperature. In addition, the desired phase NaAlSiO₄ mainly crystallize after thermal treatment and non-desired Cr₂O₃ do not crystallize. X-ray patterns of the received glass-ceramic samples treated at different temperatures and time using the glass composition 7 are presented on Fig 3. The results for crystal part of some samples, calculated from the X-ray patterns, the glass transparency evaluated microscopically and the particle size, calculated according to Sheerer equation are given in Table 2.

As can be seen, the crystallinity part and the transparency are in good agreement. Glass treated at 540°C for 4 h is 58% crystallized and transparent. Glasses treated at 560°C for 2 and 4 h are 28 and 73% crystallized respectively and transparent. Glasses treated at 560°C for 8 h and at 580°C for 4 h are 100% crystallized and opaque. So, the time treatment has a greater influence in the beginning of the crystallization. After treatment more than 4 hours the crystallization rate decreases. The opposite effect is observed in the temperature dependence – as the temperature is higher, the greater part of the glass crystallizes, but the process speed is lower up to 560°C.

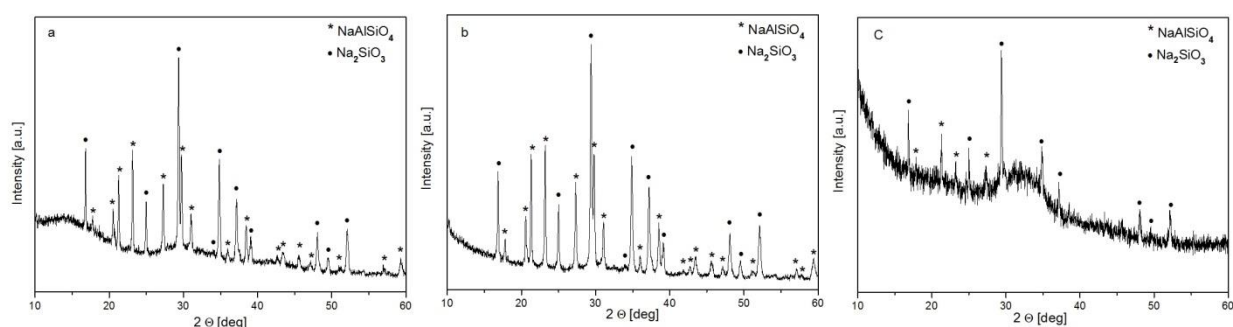


Fig. 1. XRD patterns of the glass-ceramics obtained from the glass compositions numbered 1, 2 and 4 treated at 700°C 24h (a), 600°C 24h (b) and 600°C 16h (c) respectively.

Table 1. Glass composition, thermal treatment temperatures, thermal treatment time and crystallizing phases obtained after thermal treatment.

	Glass composition [wt%]	Homogenization temperature [°C]	Duration [h]	Thermal treatment temperature [°C]	Duration [h]	Crystallized phases after thermal treatment
1.	Na ₂ O·Al ₂ O ₃ ·2SiO ₂ - Na ₂ O·SiO ₂ = 47:53 2 at% Cr Eutectic at 915°C	1300°C	3	700°C	1	glass
				700°C	24	NaAlSiO ₄ Na ₂ SiO ₃
2.	Na ₂ O·Al ₂ O ₃ ·2SiO ₂ - Na ₂ O·SiO ₂ = 47:53 5 at% Cr Eutectic at 915°C	1300°C	3	600°C	16	NaAlSiO ₄ Na ₂ SiO ₃
				600°C	24	NaAlSiO ₄ Na ₂ SiO ₃
3.	Na ₂ O:Al ₂ O ₃ :2SiO ₂ = 30:11.5:58.5 Isotherm at 768°C	No homogenization	6			
4.	Na ₂ O:Al ₂ O ₃ :2SiO ₂ = 37:13:50 5 at% Cr Isotherm 900°C	1300°C	3	600°C	16	NaAlSiO ₄ Na ₂ SiO ₃
5.	NaAlSiO ₄ -NaBO ₂ = 63:37	1100°C	24	550°C	16	NaAlSiO ₄ NaBO ₂
6.	NaAlSiO ₄ -NaBO ₂ = 66:34 5 at% Cr	1100°C	24	500°C	24	glass
				520°C	16	glass
				550°C	4	NaAlSiO ₄
					12 16	Cr ₂ O ₃
7.	NaAlSiO ₄ -NaBO ₂ = 66:34 2 at%	1100°C	24	540°C	4	NaAlSiO ₄
					8	Na ₃ B ₃ O ₆
					12	
					16	
				560°C	2	NaAlSiO ₄
					4	Na ₃ B ₃ O ₆
					8	
					12	
580°C	1	NaAlSiO ₄				
	2	Na ₃ B ₃ O ₆				
	4					
	8					

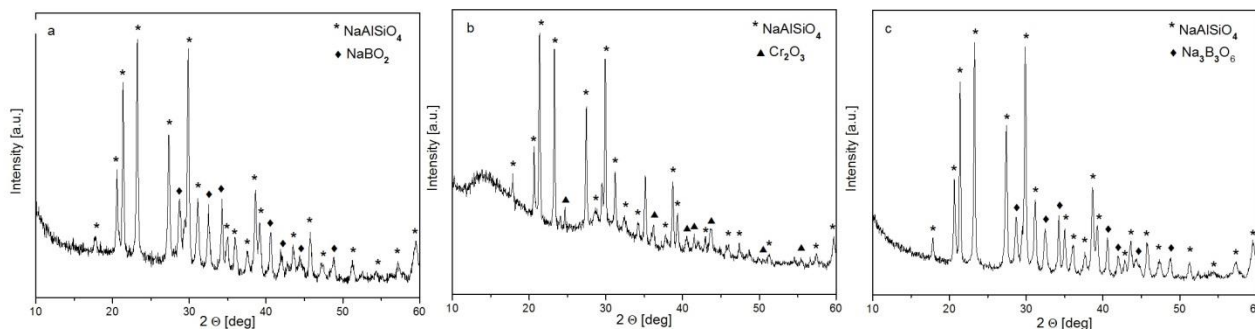


Fig. 2. XRD patterns of the glass-ceramic obtained from glass composition numbered from 5 to 7. (a) – composition 5 treated at 550°C 16h; (b) - composition 6 treated at 550°C 12h; (c) composition 7 treated at 580°C 8h.

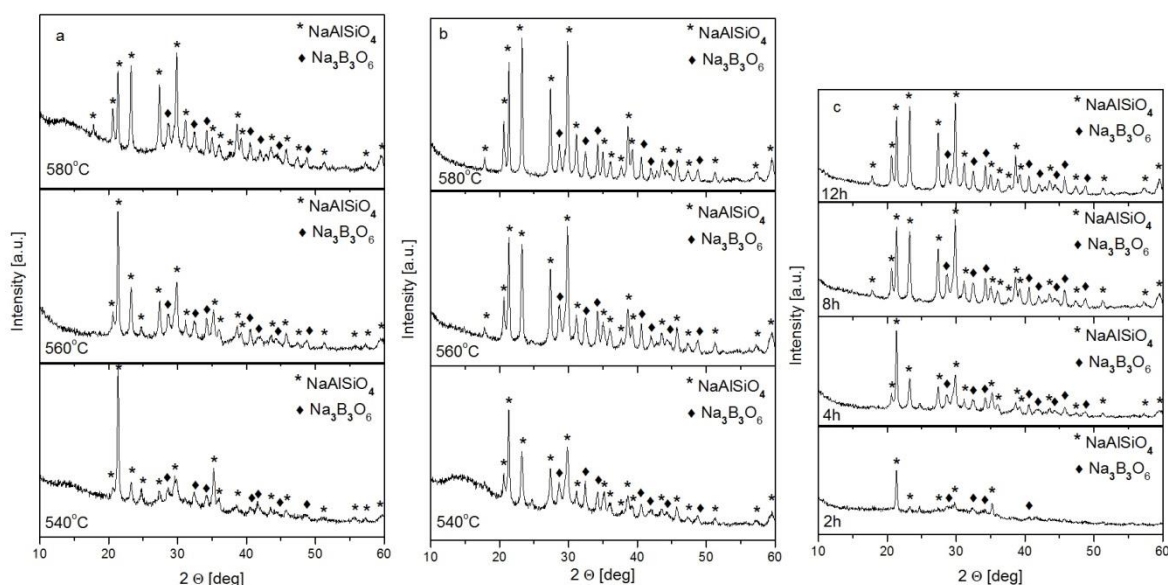


Fig. 3. XRD patterns of the glass-ceramic obtained from the glass with composition numbered 7 treated at (a) 540, 560 and 580°C during 4h; (b) 540, 560 and 580°C during 8h; (c) 560°C during 2, 4, 8 and 12h.

Table 2. Crystallinity part into the parent glass [%], transparency and particle size [nm] of the thermal treated samples:

Time °C	1	2	4	8	12	16
540			58% Transparent 45 nm	Translucent 28 nm	Opaque 34 nm	Opaque 36 nm
560		28% Transparent 30 nm	73% Transparent 35 nm	100% Opaque 35 nm	Opaque 40 nm	
580	Transparent 41 nm	Translucent 35 nm	100% Opaque 36 nm	Opaque 50 nm		

The particle size is in the range 30-50 nm and weakly depends on the temperature and the time treatment. This results show that after the beginning of the crystallization, the increasing of the time treatment or increasing the temperature leads not to

expanding of the seeds, but to arising of the new particles.

SEM micrographs of the different part of the glass-ceramic treated at 560°C during 4 hours are presented on Fig. 4 a, b, c. The particles are located predominantly on the surface of the sample. They

are relatively regular distributed between 5 and 45 nm and with an average size of 25 nm. The particle distribution is presented on Fig. 4d.

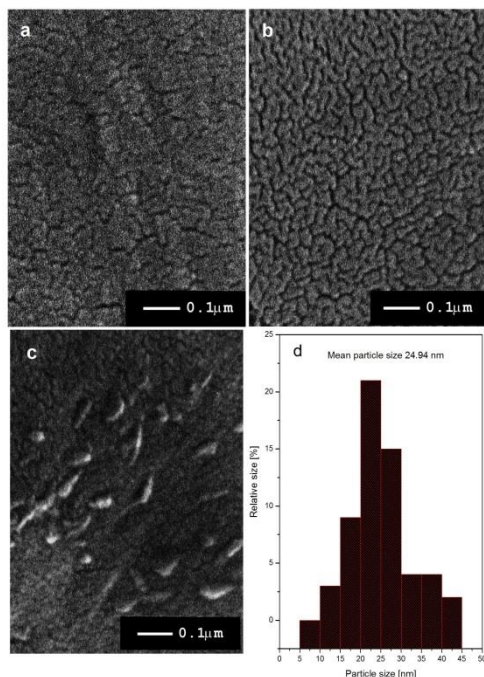


Fig. 4. SEM micrographs of the glass and different part of the glass-ceramic treated at 560°C during 4 hours: (a) – glass, (b) – center of the glass-ceramic, (c) – edge of the glass-ceramic and (d) - particle distribution and average particle size of the same glass-ceramic.

Absorption spectra of the glass and glass-ceramic samples (Fig. 5a) show similar chromium ions absorption bands belonging. The absorption spectra consist of strong absorption bands between 520 and 760 nm and the weak band near infrared absorption between 800 and 1100 nm. According to the literature [12, 29], in the region 520-800 nm the strong band is ${}^4A_2 \rightarrow {}^4T_2$ transition of the Cr^{3+} ion. Maximum in our glass and glass-ceramic is observed at 625 nm. Multiplet bands at 650 nm may be caused to the of ${}^3A_2 \rightarrow {}^3T_1$ transition of Cr^{4+} . The ${}^3A_2 \rightarrow {}^3T_1$ absorption band of the tetrahedral Cr^{4+} centers overlap with the ${}^4A_2 \rightarrow {}^4T_2$ absorption band of octahedral Cr^{3+} centers. Another band from 800 to 1100 nm is due to ${}^3A_2 \rightarrow {}^3T_2$ transition of Cr^{4+} . There is more intense absorbance in the glass-ceramic sample compared with the initial glass. So, absorption spectra show the different oxidation state of chromium ions (Cr^{3+} and Cr^{4+}).

The emission spectra (Fig. 5b) overlap from 1000 to 1500 nm. There is a strong peak at 1067 nm and a weak and wide one at 1340 nm. The emission spectra shows different oxidation states of the chromium ions in the glass-ceramic samples. In accordance to the absorption spectra the first

emission peak could be attributed to ${}^4T_2 \rightarrow {}^4A_2$ of Cr^{3+} ions and second peak is attributed to ${}^3T_2 \rightarrow {}^3A_2$ of Cr^{4+} in tetrahedral occupation. Such summarized emission spectra is expected [12, 30], taking into account the existence of three matrix (residual glass, $NaAlSiO_4$ and $Na_3B_3O_6$), where the chromium ion could be incorporated.

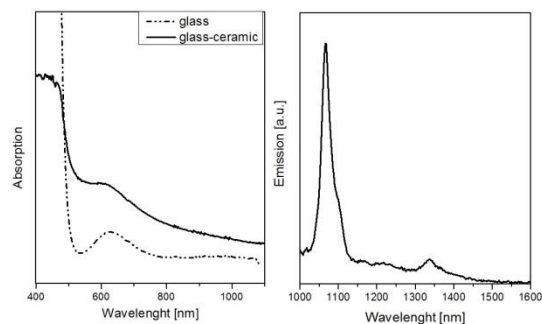


Fig. 5. Absorption and emission spectra of the glass-ceramic samples obtained from the glass with composition numbered 7 treated at 580°C for 1 hour.

CONCLUSION

Pure and chromium doped homogeneous glasses from the systems $Na_2O-Al_2O_3-SiO_2$ and $Na_2O-Al_2O_3-SiO_2-NaBO_2$ are prepared. Transparent 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. In all thermal regimes $NaAlSiO_4$ appears. Except $NaAlSiO_4$, different phases crystallize depending on the glass-composition and treatment conditions. The glass-ceramics are transparent to the crystallization degree of about 75%. The mean particle size is about 25 nm and weak depends on the thermal treatment time and the thermal treatment temperature. Absorption and emission spectra of the sample with crystallizing phases $NaAlSiO_4$ and $Na_3B_3O_6$ doped by 2 at% Cr show co-existing of the Cr^{3+} and Cr^{4+} ions and are discussed in the terms of Cr^{3+} and Cr^{4+} ions.

REFERENCES

1. V. Petričević, S. Gayen, R. Alfano, K. Yamagishi, H. Anzai, Y. Yamaguchi, *Appl. Phys. Lett.*, **52**, 1040 (1988).
2. H. R. Verdun, L. M. Thomas, D. M. Andrauskas, T. McCollum, A. Pinto, *Appl. Phys. Lett.*, **53**, 2593 (1988).
3. L. Yang, V. Petricevic, R. R. Alfano, in: Novel laser sources and applications: Proc. workshop, Nov.12-13, 1993, San Jose, California, USA, 1993, p. 103.

4. R. Alfano, A. Bykov, V. Petricevic, US Patent 7,440,480 (2008).
5. A. Bykov, V. Petricevic, J. Steiner, Di Yao, L. Isaacs, M. Kokta, R. Alfano, J. Cryst. Growth, 211, 295 (2000).
6. K. Subbotin, E. Zharikov, L. Iskhakova and S. V. Lavrishchev, *Crystallogr. Rep.*, **46**, 1030 (2001).
7. K. Subbotin, L. Iskhakova, E. Zharikov, S. Lavrishchev, *Crystallogr. Rep.*, **53**, 1107 (2008).
8. C. Anino; J. Thery, D. Vivien, in Tunable Solid State Lasers, Intern. Soc. Optics and Photonics, 1997, p. 38.
9. A. Sugimoto, Y. Nobe, K. Yamagishi, *J. Cryst. Growth* **140**, 349 (1994).
10. M. Jazi, M. D. Baghi, M. Hajimahmodzadeh, M. Soltanolkotabi, *Optics & Laser Technol.*, **44**, 522 (2012).
11. A. Ulyashenko, N. Nikonorov, A. Przhhevuskii, *B. Russ. Acad. Sci.: Physics*, **71**, 159 (2007).
12. M. Sharonov, A. Bykov, T. Myint, V. Petricevic, R. Alfano, *Opt. Commun.*, **275**, 123 (2007).
13. K. Subbotin, V. Smirnov, E. Zharikov, L. Iskhakova, V. Senin, V. Voronov, I. Shcherbakov, *Opt. Mater.*, **32**, 896 (2010).
14. K. Subbotin, S. Arakelian, V. Voronov, V. Senin, M. Gerke, V. Smirnov, D. Nikolaev, E. Zharikov, I. Shcherbakov, *J. Cryst. Growth*, **328**, 95 (2011).
15. Y. Zhuang, Y. Teng, J. Luo, B. Zhu, Y. Chi, E. Wu, H. Zeng, J. Qiu, *Appl. Phys. Lett.*, **95**, 111913 (2009).
16. D. Deng, S. Xu, H. Ju, S. Zhao, H. Wang, C. Li, *Chem. Phys. Lett.*, **486**, 126 (2010).
17. J. Dong, K. Ueda, A. Shirakawa, H. Yagi, T. Yanagitani, A. A. Kaminskii, *Opt. Express*, **15**, 14516 (2007).
18. T. Hahn, M. Buerger, *Z. Kristallogr.*, **106**, 308 (1955).
19. K. Tait, E. Sokolova, F. Hawthorne, *The Can. Mineral.*, **41**, 61 (2003).
20. C.M.B. Henderson, J. Roux, *Contrib. Mineral. Petr.*, 61, 279 (1977).
21. C. Henderson, A. Thompson, *Am. Mineral.*, **65**, 970 (1980).
22. H. Schneider, O. Flörke, R. Stoock, *Z. Kristallogr.*, **209**, 113 (1994).
23. M. Hirose, T. Kobayashi, K. Maeda, *Reports Res. Lab. Asahi Glass Co., Ltd.*, **55** (2005).
24. E. Hamzawya, E. El-Meliegy, *Mater. Chem. Phys.*, **112**, 432 (2008).
25. M. Wang, N. Wu, M. Hon, *Mater. Chem. Phys.*, **37**, 370 (1994).
26. J. Mac Dowell, *J. Am. Ceram. Soc.* **58**, 258 (1975).
27. E. Levin, *Phase Diagrams for Ceramists*, Columbus, Ohio: American Ceramic Society, (1956), p. 96.
28. G. Kostorz, H. Herman. *Phase diagrams in advanced Ceramics*. Ed. Allen M. Alper, Elsevier, 1995.
29. C. Jousseume, D. Vivien, A. Kahn-Harari, B.Z. Malkin, *Opt. Mater.*, **24**, 143 (2003).
30. S. Morimoto, *J. Ceram. Soc. Jpn.*, **112**, 486 (2004).

ПОЛУЧАВАНЕ НА ДОТИРАНА С ХРОМ СЪТЪКЛОКЕРАМИКА СЪДЪРЖАЩА NaAlSiO_4 И $\text{Na}_3\text{B}_3\text{O}_6$

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(Резюме)

Синтезирани са чисти и дотирани с хром хомогенни стъкла от системите $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ и $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3$. Прозрачни стъклокерамики са получени след термично третиране на стъклата при различни температури и с различна продължителност. Определени са кристализиращите фази, степента на кристализация и размерът на частиците. Представени са спектри на абсорбция и емисия за стъклокерамични образци с кристализиращи фази NaAlSiO_4 и $\text{Na}_3\text{B}_3\text{O}_6$. Спектрите показват едновременното присъствие на йони Cr^{3+} и Cr^{4+} и са обсъдени от гледна точка на енергетичните нива на йоните Cr^{3+} и Cr^{4+} .