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Study of Glass Ceramics with $YNbO_4:Tb^{3+}$ Crystallites Synthesized at Different Temperatures

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Received July 11, 2022
Revised September 18, 2022 Accepted September 19, 2022

The optimal temperature regime for the synthesis of glass ceramics with $YNbO_4:Tb^{3+}$ crystalline inclusions has been established. Glass ceramics were synthesized on the basis of a sodium borate matrix from oxide precursors. It has been established that synthesis at a temperature of 950°C is optimal, since at this temperature only one crystalline phase $YNbO_4:Tb^{3+}$ is formed in the glass and its content is maximum. The spectra of crystalline inclusions and the glass matrix were obtained by the method of local cathodoluminescence, the phase composition of glass ceramics was studied by X-ray phase analysis.

Keywords: $YNbO_4$, luminescence, terbium ion, glass ceramics.

DOI: 10.21883/EOS.2022.11.55104.3911-22

Introduction

The search for and development of new effective luminophors remains an urgent task due to their wide application in various fields of science, technology and medicine [1,2]. One of the most promising lines of research is the development of glass-ceramic materials with crystalline inclusions of oxides activated by rare-earth ions (REIs), including rare-earth niobates. Yttrium niobate activated by REIs is a promising radiation-resistant scintillator, in particular, an X-ray luminophor. Such hybrid materials combine the properties of both glasses and crystals. Their synthesis and subsequent treatment are similar to the synthesis and treatment of glass, while the level of nonradiative losses during luminescence excitation are much lower than in all-amorphous materials. In the course of previous studies [3–5] it was found that the boron sodium oxide matrix is extremely promising for the low-temperature synthesis of REI-doped yttrium niobate.

The purpose of this work was to study the influence of the synthesis temperature on the phase composition and luminescent properties of glass ceramics based on a sodium boron matrix with crystalline inclusions of yttrium niobate. The rare-earth ion Tb^{3+} was used as an activator in this work. Tb^{3+} ions in $YNbO_4$ crystals exhibit intense luminescence in the green range of the spectrum associated with energy transitions from level $^5D_4$.

Sample synthesis

For the synthesis of glass ceramics, a sodium-boron matrix was chosen, since it proved to be the most promising for the synthesis of glass ceramics with $YNbO_4$ [3,4]. Yttrium, niobium, and terbium compounds were added to the matrix in such a proportion that the following molar ratios in terms of oxides were met in the synthesized material: $M(Tb_2O_3)/M(Y_2O_3) \leq 0.2$ and $M(Tb_2O_3 + Y_2O_3)/M(Nb_2O_5) \sim 1$. To form crystallites in the material at the final stage of synthesis, the samples were slowly cooled in a muffle furnace. Reagents with a purity of at least 99% were used as initial components for melting glasses.

For the synthesis of all samples, an oxide multicomponent mixture was prepared with the following composition (wt.%): $7.2Y_2O_3 - 12Nb_2O_5 - 2.4Tb_4O_7 - 78.4Na_2B_4O_7$. The mixture was ground in a mortar. Sintering was carried out in a ceramic crucible. For all samples, the charging material heating time was 1 h, holding at the maximum temperature was 30 min. The samples were cooled to room temperature for 3.5 h. The sintering temperature for all samples was different and amounted to 900, 950, 1000 and 1050°C (Table 1).

Research methods

The homogeneity of the samples, the presence of inclusions, the cathodoluminescent properties of the inclusions and the glass matrix were measured on a CAMEBAX electron probe microanalyzer (Cameca, France) equipped with an optical microscope and combined with a cathodoluminescent station of the original design [6]. The instrument makes it possible to obtain optical images of a sample in reflected light, cathodoluminescent images in wide electron

Table 1. Samples under study and their sintering temperature

№ of sample	Sample designation	Sintering temperature, °C
1	Bura-Tb-900	900
2	Bura-Tb-950	950
3	Bura-Tb-1000	1000
4	Bura-Tb-1050	1050

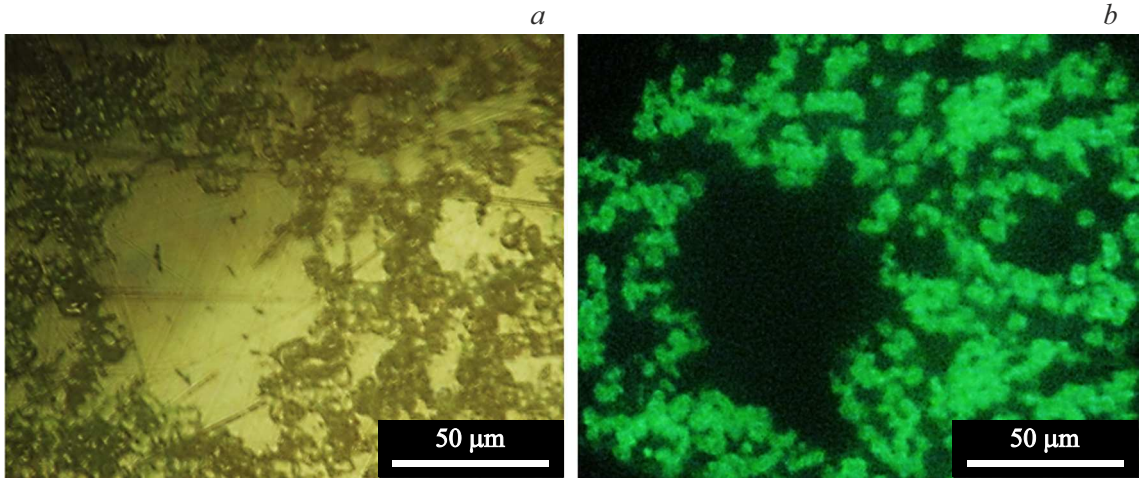

Figure 1. Images obtained by optical microscopy (*a*) and cathodoluminescence microscopy (*b*) for Bura-Tb-900 sample.

beam (up to 200 μm) and register cathodoluminescent (CL) radiation spectra with lateral resolution from 1 μm. The CL spectra were obtained at electron accelerating voltage of 20 kV, absorbed current of 20 nA and an electron beam diameter of 3 μm. CL images were obtained with electron beam diameter of 200 μm, accelerating voltage of electrons equal to 20 kV, and absorbed current of 100 nA.

The phase composition of the samples and the coherent scattering region (CSR) of the crystalline phases were determined by X-ray diffraction (XRD) phase analysis on a D8 Discover X-ray diffractometer (Bruker, Germany). The weight content of crystalline phases was calculated from diffraction curves using the Topas 5 software package. The detection threshold for crystalline phases in a material is 0.5 wt.%.

Results and discussion. Results of X-ray phase analysis

The diffraction patterns of all samples show a broad „halo", whose maximum position is characteristic of sodium borate glass, and narrow peaks corresponding to crystalline phases. It was found that each of the samples contained crystalline inclusions. The obtained diffraction curves are similar in nature to the results presented in the work [4]. The results of XRD analysis of the samples are presented in Table 2.

Optical and cathodoluminescent microscopy, CL spectra

Figure 1 shows images of the same region of the Bura-Tb-900 sample obtained by optical (Fig. 1, *a*) and cathodoluminescent (Fig. 1, it b) microscopy. Both images show a contrast that is characteristic of micron-sized crystalline inclusions. The size of the inclusions significantly exceeds the

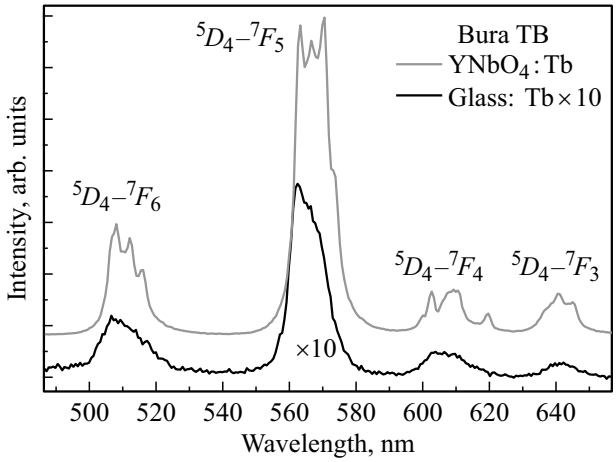

Figure 2. CL spectra of Bura-Tb-900 sample.

CSR calculated from the diffraction curves (Table 1). This suggests that micron-sized inclusions of crystalline material observed in optical and cathodoluminescence images are particle clusters or polycrystals with a CSR of 30–40 nm in size. The resulting images are typical for all Bura-Tb-X samples.

Fig. 2 shows the CL spectra, which are typical for all Bura-Tb-X samples. The CL spectra in Fig. 2 (gray curve) were obtained in regions with crystalline inclusions. The shape of the spectrum corresponds to the luminescence spectrum of Tb^{3+} in $YNbO_4$, where rare-earth ions (including Tb^{3+}) occupy the local positions C_2 [3,7,8]. This confirms the results obtained by the XRD. The low-intensity spectrum in Fig. 2 (black curve) is typical for a terbium-activated amorphous matrix, where Tb^{3+} ions occupy local positions C_2 [9,10]. The energy transitions of the Tb^{3+} ion are indicated on the CL spectra.

Table 2. XRD analysis of the crystalline phase of the samples

Pattern	Identified crystalline phase	Content of crystalline phase in the sample, wt.%	Region of coherent scattering, nm
Bura-Tb-900	M-$YNbO_4$	$\geq 82 \pm 3$	30 ± 3
	$NaNbO_3$	$\leq 2 \pm 1$	–
	$Na_2B_4O_7$	$\leq 1 \pm 0.5$	–
Bura-Tb-950	M-$YNbO_4$	80 ± 3	35 ± 3
Bura-Tb-1000	M-$YNbO_4$	75 ± 3	35 ± 3
Bura-Tb-1050	M-$YNbO_4$	70 ± 3	40 ± 4

Conclusions

Thus, for the first time ever, low-temperature glass ceramics based on a sodium borate matrix with $YNbO_4$ crystallites doped with Tb^{3+} have been synthesized. It was found that at this stage of studies, synthesis at temperatures above 950°C is optimal, since in this case only the $YNbO_4:Tb^{3+}$ phase is formed in the glass. The size of the $YNbO_4:Tb^{3+}$ crystalline phase inclusions, according to optical and cathodoluminescence microscopy data, is several micrometers. These inclusions are particle clusters or polycrystals with CSR of 30–40 nm in size.

Acknowledgments

The authors are grateful to M.I. Moskvichev and V.V. Vaskevich for the samples provided and to M.A. Yagovkina for XRD studies performed.

Funding

XDPstudies were performed using the equipment of the Federal Common Research Center „Materials Science and Diagnostics in Advanced Technologies“, supported by the Ministry of Education and Science of Russia (unique project identifier: RFMEFI62119X0021).The authors are grateful to M.I. Moskvichev and V.V. Vaskevich for the samples provided and to M.A. studies. Yagovkina for XRD studies performed.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.Yu. Mester, A.M. Mozharov, A.N. Trofimov, M.V. Zamoryanskaya. Opt. i spektr., 120 (5), 768 (2016). (in Russian).
DOI: 10.7868/S0030403416050196A
[A.Y. Mester, A.M. Mozharov, A.N. Trofimov, M.V. Zamoryanskaya. Opt. Spectrosc., **120** (5), 726 (2016)].
DOI: 10.1134/S0030400X16050192

[2] M. Nazarov, Y.J. Kim, E.Y. Lee, K.I. Min, M.S. Jeong, S.W. Lee, D.Y. Noh. J. Appl. Phys., **107**, 103104 (2010).
DOI: 10.1063/1.3392918

[3] V.A. Kravets, E.V. Ivanova, K.N. Orekhova, G.A. Gusev, V.V. Vaskevich, M.I. Moskvichev, M.V. Zamoryanskaya. Opt. i spektr., **129** (2), 207 (2021) (in Russian).
DOI: 10.21883/OS.2021.02.50559.179-20 [V.A. Kravets, E.V. Ivanova, K.N. Orekhova, G.A. Gusev, V.V. Vas'kevich, M.I. Moskvichev, M.V. Zamoryanskaya. Opt. Spectrosc., **129** (2), 245 (2021)]. DOI: 10.1134/S0030400X21020077

[4] V.A. Kravets, E.V. Ivanova, M.A. Yagovkina, M.V. Zamoryanskaya. Opt. i spektr., **129** (1417), 1423 (2021) (in Russian).
DOI: 10.21883/OS.2021.11.51642.2083-21

[5] V.A. Kravets, E.V. Ivanova, M.V. Zamoryanskaya. J. Physics: Conference Series, **1697**, 012163 (2020).

[6] M.V. Zamoryanskaya, S.G. Konnikov, A.N. Zamoryanskii. Instrum. Exp. Tech., **47**, 477–483 (2004).
DOI: 10.1023/B:INET.0000038392.08043.d6

[7] X. Liu, Y. Lü, C. Chen, S. Luo, Y. Zeng, X. Zhang, J. Lin. J. Phys. Chem. C, **118** (47), 27516–27524 (2014).
DOI: 10.1016/j.cej.2016.03.149

[8] P. Boutinaud, E. Cavalli, M. Bettinelli. J. Phys.: Condensed Matter., **19** (38), 386230 (2007).

[9] V.A. Kravets, E.V. Ivanova, K.N. Orekhova, M.A. Petrova, G.A. Gusev, A. N. Trofimov, M.V. Zamoryanskaya. J. Lumines., **226**, 117419 (2020).
DOI: 10.1016/j.jlumin.2020.117419

[10] N. Wada, K. Kojima. Optical Materials., **35** (11), 1908 (2013).
DOI: 10.1016/j.optmat.2013.01.008