The study of gadolinium tantalum niobate \((\text{Gd(Nb}_x\text{Ta}_{1-x})\text{O}_4)\) by local cathodoluminescence technique

G A Gusev\(^1\), S M Masloboeva\(^2\) and M V Zamoryanskaya\(^1\)

\(^1\)Ioffe Institute, Politekhnicheskaya ul. 26, Saint Petersburg, 194021 Russia
\(^2\)Tananaev Institute of Chemistry - Subdivision of the Federal Research Centre «Kola Science Centre of the Russian Academy of Sciences» Science Centre of Russian Academy of Sciences, «Academic town» 26a, Apatity, Murmansk region, 184209 Russia

E-mail: ggusev@mail.ioffe.ru

Abstract. In this work, the powder and ceramic samples of gadolinium tantalum niobate \((\text{Gd(Nb}_x\text{Ta}_{1-x})\text{O}_4)\) grown by the liquid-phase method were studied. Phase homogeneity and composition were determined by x-ray diffraction analysis and electron probe microanalysis. Luminescent properties were studied by local cathodoluminescence technique. All samples obtained had a high phase homogeneity. It was found that the dependence of the monoclinic lattice parameters on the niobium content in the niobium-tantalum pair has monotonic character. The solid solutions were formed at synthesis temperatures from 1180 to 1400 °C. The sample of pure gadolinium niobate \((\text{GdNbO}_4)\) showed the maximal cathodoluminescence intensity.

1. Introduction

The development of new effective scintillators is an important practical task. Materials, which convert high-energy excitation (irradiation with α-particles, neutrons, electrons; x-ray and gamma radiation) into visible light, are widely used to create sensors in dosimetry, medicine, science and the security field [1-3].

The creation of scintillators based on heavy metal oxides is one of the current research directions [4-6]. Such materials have good chemical and physical stability, which allows to use them in aggressive environmental conditions. However, such scintillators have a relatively low light yield in comparison to widely known scintillators, such as CsI(Tl), NaI(Tl), etc. It is possible to increase light yield, by using the phenomenon of emitting centers sensitization [7], for example, when the excitation is transferred from intrinsic defects to luminescence centers. Therefore, scintillators based on heavy metal oxides with intense intrinsic luminescence, such as rare earth tantalates and niobates are of great interest [8-10]. Rare earth niobates have bright intrinsic luminescence [11], and rare-earth tantalates have high density and high stopping power [12]. It was proposed to create rare-earth tantalum niobate solid solution \((\text{ReNb}_x\text{Ta}_{1-x}\text{O}_4)\) [13, 14] on an analogy with other systems studied [15, 16] to combine and improve the scintillation properties of these materials.

The solid-phase method is the most widely used method for \(\text{ReNb}_x\text{Ta}_{1-x}\text{O}_4\) synthesis. It includes stages of grinding mixtures of oxides and long-term annealing at temperatures of more than 1500 °C [14]. The liquid-phase synthesis method, used in this work, does not imply a stage of mechanical grinding of the components, and it ensures the homogenization of components at the molecular level, which provides a more exact adherence to the specified element ratio of the solid solution [17].
addition, the annealing temperatures used in this method do not exceed 1400 °C. Liquid-phase method allows the synthesis of high-homogeneity powders for further use as phosphors or for ceramics producing.

The purpose of this work was to determine the optimal niobium-tantalum ratio for the maximum luminescence light yield in gadolinium tantalum-niobate samples synthesized by an improved liquid-phase method.

2. Samples and methods
The method of liquid-phase synthesis was described in detail in work [17]. High-purity fluoride Nb and Ta-containing solutions were mixed in a given volume ratio to obtain crystalline powders of gadolinium tantalum niobate of various compositions. Then, an ammonia co-precipitation of niobium and tantalum hydroxides was carried out, and after washing the precipitate from fluorine, it was mixed with a solution of gadolinium nitrate Gd(NO$_3$)$_3$ in a volume corresponding to the calculated value and brought to pH ~ 8 by adding an ammonia solution. After precipitation of the resulting pulp, the filtration and washing steps were followed. The synthesis process was completed by sequential calcination at temperatures up to 1400 °C, and, starting from ~ 700 °C, powder grinding was carried out in stages in a MK 1 chalcedony ball mill. Two series of GdNb$_x$Ta$_{1-x}$O$_4$ powders (calcining temperatures of 1180 °C and 1400 °C) with the planned value x = 0 ÷ 1 were obtained using such method. In comparison to the earlier work [17], the optimization of the liquid-phase synthesis method was carried out and the powder calcination scheme was changed, which, in our opinion, should have increased the phase-homogeneity of the synthesized materials and provided the formation of solid solutions at lower temperatures.

Ceramic samples were pressed in the form of tablets from powders synthesized at 1180 °C. Polyvinyl alcohol was used as a binder. Compression of the tablets was carried out at P ~ 3.8 kg/cm$^2$. The tablets were kept in a Nabetherm GmbH electrical resistance furnace at 1400 °C for 5 hours.

The phase composition and structural parameters were studied by x-ray diffraction analysis (XRD). The studies were performed with a 2D Phaser Bruker (Germany) diffractometer (Cu Kα radiation wavelength $\lambda$ = 1.5406 Å, at 30 kV and 10 mA), using a PSD detector. Unit cell parameters were determined by the internal standard method (puriss. NaCl). The phase identification was based on the ICDD database (PDF 2, release 2014).

The elemental composition of the samples was determined by electron probe microanalysis (EPMA). The luminescent properties were studied by local cathodoluminescence technique (CL). A Camebax (France) electron probe microanalyzer equipped with four X-ray wavelength-dispersive spectrometers and an optical spectrometer was used for measurements [18]. The powder samples were pressed into indium, and the ceramic samples were fixed in the Wood alloy to perform the studies. All samples were additionally covered with a carbon film using the JEE-4C vacuum station (Jeol, Japan) to ensure charge drainage during the electron probe studies.

EPMA measurements were carried out at an accelerating voltage of 20 kV and an absorbed current of 10 nA. Pure metal samples of Ta (Lα characteristic X-ray line) and Nb (Lα), and GdPO$_4$ (Lα) were used as EPMA standards. The oxygen content was calculated by stoichiometry. The CL spectra were excited by an electron beam with a diameter of 4 μm, an absorbed current of 17 nA, and an accelerating voltage of 20 kV.

3. Results and Discussion
According to XRD results, all series of samples formed solid solutions of Gd(Nb$_x$Ta$_{1-x}$)O$_4$ with an isomorphic (Nb-Ta) substitution. Samples with x = 0.5–1 had a monoclinic structure corresponding to GdNbO$_4$. The content of impurity phases (Gd$_3$NbO$_7$, Gd$_2$O$_3$, etc.) was less than 7%. Samples with x = 0-0.3 had a monoclinic structure corresponding to GdTaO$_4$, and the content of other phases did not exceed 10%. In both powders and ceramics, the monotonic nature of the monoclinic lattice parameters dependence on the niobium content was observed (Figure 1). An exception was a powder sample with a value of x = 0 synthesized at 1180 °C. It had a different structural polytype (with a multiple of 0.5 parameter b) that did not fit into the monotonic dependence of the other samples parameters.
EPMA showed that the deviation of the elemental composition at different measured points from the average value for a particular ceramic sample is less than 7%. At the same time, the deviation of the average measured value of the formula unit (x) for each sample of solid solutions from the planned one was no more than 12%.

![Graph showing lattice parameters](image)

**Figure 1.** Dependence of the lattice parameters (a, b, c) of ceramic GdNb$_x$Ta$_{1-x}$O$_4$ samples on the Nb content (by EPMA). The red dots correspond to the reference lattice parameters for GdNbO$_4$ and GdTaO$_4$ taken from the ICDD database.

CL spectra were obtained for all ceramic samples at a room temperature (Figure 2). The maximum luminescence intensity was observed for the sample with x = 1 (inset in Figure 2). This data coincided with the results obtained using solid-phase synthesis [14]. CL band maximum intensity for samples containing Nb corresponded to wavelengths of 442 - 451 nm. For pure gadolinium tantalate it was 543 nm. Also, at wavelengths of 312 nm, peaks associated with the transition in the Gd$^{3+}$ ion were observed. In addition, narrow CL bands (at ~ 613, ~ 626 nm) were present in the spectra. According to their position, it can be assumed that these were emission bands of europium ions (Eu$^{3+}$). This can be explained by contamination of the samples with trace amounts of europium at the synthesis stage. CL band with 450 nm maximum intensity dependence on the niobium content in ceramic samples is shown in the inset in Figure 2.
Figure 2. CL spectra of ceramic samples GdNb$_x$Ta$_{1-x}$O$_4$. 1) x = 0, 2) x = 0.3, 3) x = 0.5, 4) x = 0.7, 5) x = 0.9, 6) x = 1. The inset shows the dependence of the luminescence intensity on the Nb content.

4. Conclusions
Phase-homogeneous gadolinium tantalum-niobate powders were obtained by the liquid-phase synthesis method. The GdNb$_x$Ta$_{1-x}$O$_4$ solid solution was formed at temperatures from 1180 to 1400 °C. The monotonic nature of the monoclinic lattice parameters dependence on the niobium content in the niobium-tantalum pair was observed for almost all samples. The sample of pure gadolinium niobate (GdNbO$_4$) showed the maximal cathodoluminescence intensity.

Acknowledgements
Authors are grateful to T.B. Popova for the help in EPMA study and grateful to M.A. Yagovkina for the XRD measurements. XRD and structural studies were performed using the equipment of the Joint Research Center ‘Material science and characterization in advanced technology’. The reported study was funded by RFBR according to the research project №19-33-50149.

References
[1] Yanagida T 2018 Proc. Jpn. Acad., Ser. B 94 75-97
[2] Glodo J, Wang Y, Shawgo R, Brecher C, Hawrami R H, Tower J and Shah K S 2017 Phys. Procedia 90 285-90
[3] Lecoq P, Gektin A and Korzhik M 2017 Inorganic scintillators for detector systems (Springer International Publishing, Switzerland) p 420
[4] Nikl M and Yoshikawa A 2015 Adv. Opt. Mater. 3 463-81
[5] Dujardin C, Auffray E, Bourret-Courchesne E, Dorenbos P, Lecoq P, Nikl M, Vasil’ev A N, Yoshikawa A and Zhu R Y 2018 IEEE Trans. Nucl. Sci. 68 1977-97
[6] Stanek C R, McClellan K J, Levy M R and Grimes R W 2006 J. Appl. Phys. 99 113518
[7] Nazarov M V, Jeon D Y, Kang J H, Popovici E J, Muresan L E, Zamoryanskaya M V and Tsukerblat B S 2004 Solid State Commun. 131 307-11
[8] Arellano I, Nazarov M, Byeon C C, Popovici E J, Kim H and Kang H C 2010 Mater. Chem. Phys. 119 48-51
[9] Hwang M H and Kim Y J 2008 Ceram. Int. 34 1117-20
[10] Lü Y, Chen C, Li S, Liu X, Yan L, Dai Y, Zhang A, Xie Y and Tang X 2015 Eur. J. Inorg. Chem. 2015 5262-71
[11] Lee S K, Chang H, Han C H, Kim H J, Jang H G and Park H D 2001 J. Solid State Chem. 156 267-73
[12] Su M Z and Zhao W 2005 Spectroscopic Properties of Rare Earths in Optical Materials (Springer, Berlin) pp. 500-29
[13] Voloshyna O V, Boiaryntseva I A, Baumer V N, Ivanov A I, Korjik M V and Sidletskiy O T 2014 Nucl. Instrum. Methods Phys. Res., Sect. A 764 227-31
[14] Voloshyna O, Sidletskiy O, Spassky D, Gerasymov I, Romet I and Belsky A 2018 Opt. Mater. 76 382-87
[15] Sidletskiy O 2018 Phys. Status Solidi A 215 1701034
[16] Kamada K, Endo T, Tsutumi K, Yanagida T, Fujimoto Y, Fukabori A, Yoshikawa A, Pejchal J and Nikl M 2011 Cryst. Growth Des. 11 4484-90
[17] Ivanova E V, Masloboeva S M, Kravets V A, Orekhova K N, Gusev G A, Trofimov A N, Shcherbina O B, Yagovkina M A, Averin A A and Zamoryanskaya M V 2019 Opt. Spectrosc. 127 1011-17
[18] Zamoryanskaya M V, Konnikov S G, Zamoryanskii A N 2004 Instrum. Exp. Tech. 47 477–83