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Synthesis and study of the luminescent properties of terbium-activated gadolinium tantalum-niobate

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For the first time, terbium-activated gadolinium tantalo-niobates were synthesized ($(Gd_{1-x}Tb_x)Nb_yTa_{1-y}O_4$). The synthesis was carried out by the liquid-phase method. All studied materials had the main crystalline modification M $GdNbO_4$. The content of impurity phases did not exceed 2−5%. The photo- and cathodoluminescence spectra were studied. Concentration quenching of the terbium ion luminescence for a series of solid solutions containing tantalum ($(Gd_{1-x}Tb_x)Nb_{0.9}Ta_{0.1}O_4$) occurs earlier than for pure gadolinium niobates ($(Gd_{1-x}Tb_x)NbO_4$). The obtained materials are promising for use as scintillators.

Keywords: gadolinium tantalum-niobates, liquid-phase synthesis, Tb^{3+}, luminescence, cathodoluminescence.

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Introduction

Niobates ($LnNbO_4$) and tantalates ($LnTaO_4$) of rare earth elements, both activated and non-activated by rare earth ions (REI), are promising functional materials. These substances are widely used as luminophores and laser crystals [1], X-ray detectors [2] and scintillators in television panels [3]. Their use is due to luminescent and photoelectronic properties, high physical and chemical resistance [4].

One of the most important properties of such compounds is the presence of an intrinsic luminescence band in the blue range of the spectrum. It is associated with the NbO_4 or TaO_4 complexes in niobates or tantalates, respectively [5]. The energy levels of these complexes can sensitize the luminescence of emitting centers such as REIs. The average atomic number of a substance is also an important parameter for the practical application of a compound as a scintillator [6]. The higher the atomic number, the greater the ability of a given scintillator to absorb high-energy radiation. In this regard, gadolinium niobate deserves special attention. It has a bright intrinsic luminescence and a higher average atomic number than, for example, the widely used yttrium niobate. At the same time, gadolinium tantalate is one of the densest known scintillators. However, it has a much weaker intrinsic luminescence yield compared to $GdNbO_4$ [7]. Therefore, it seems promising to replace part of the niobium in $GdNbO_4$ with tantalum in order to increase the average atomic number of the substance, but at the same time retain the luminescent properties of gadolinium niobate.

Solid solutions of gadolinium tantalum-niobates have been studied in a number of articles [7,8]. Thus, it was shown that the intermediate solid solution of $GdNb_xTa_{1-x}O_4$ has a higher luminescence yield compared to $GdNbO_4$ at low temperature [7]. It was also demonstrated that the $GdTa_{0.8}Nb_{0.2}O_4$ solid solution has attenuation times with a very short dominant component ~ 17 ns [9]. Such properties make gadolinium tantalum-niobate a promising scintillator.

Addition of REIs to niobates and tantalates has been considered in a number of publications [2,3,10–12]. However, studies of activated $GdNb_xTa_{1-x}O_4$ solid solutions are almost non-existent. It has been shown that the activation of gadolinium tantalo-niobate with europium produces a material with bright red luminescence. This substance is promising for use as a detector of high-energy radiation [13]. In this connection, it seems interesting to implement the scheme of additional sensitization of europium with terbium. Such a bunch of REIs is widely used in other materials [14]. In addition, activation of $GdNb_xTa_{1-x}O_4$ with terbium can give a material with bright green luminescence, which in itself can be of practical interest. Such a compound has not been previously synthesized and its luminescent properties have not been studied.

The most widely used method for obtaining niobates, tantalates and their solid solutions is solid-phase synthesis [9]. However, with this approach, there are losses at the stage of mechanical grinding of the components, and long-term annealing is used at temperatures from 1400°C. In this article, we used a method based on the liquid-phase synthesis of tantalum-niobates of rare earth elements [13,15].

It made it possible to homogenize the components at the molecular level, and therefore more accurately follow the given composition. In addition, the temperatures used in this method do not exceed 1400°C.

The purpose of this article was to synthesize and study the structural, luminescent properties of gadolinium tantalum niobate ceramics activated with terbium, a promising scintillation material.

Materials and research techniques

In this article, ceramic samples $(Gd_{1-x}Tb_x)Nb_yTa_{1-y}O_4$, where $x = 0.05{-}0.2$; $y = 0.9$, 1, were studied. Powders for obtaining this ceramics were synthesized by a method based on liquid-phase synthesis [13,16].

For the synthesis, high-purity niobium- and tantalum-containing fluoride solutions were used, which were obtained by dissolving oxides Nb_2O_5 (extra-pure grade) and Ta_2O_5 (extra-pure grade) in HF (extra-pure grade). The composition of the solutions corresponded (in units of $g \cdot l^{-1}$): Nb_2O_5 — 146.0, F^- — 132.7; Ta_2O_5 — 109.3, F^- — 105.0. When preparing tantalum niobates, Nb and Ta solutions were mixed with each other in volumes that ensured the specified composition of the samples under study. 25%- solution of NH_4OH (extra-pure grade) was introduced into Nb-, Ta-containing solutions or their mixtures, and niobium and tantalum hydroxides were precipitated up to pH ∼ 9–10. The precipitate was filtered on a Nutsche- filter and then washed three times by repulping with deionized water to remove ammonium and fluorine ions at a ratio of solid and liquid phases of 1:3. The residue, dried to a moisture content of 60–70% at 90°C, was mixed with solutions of $Gd(NO_3)_3$ and $Tb(NO_3)_3$, the volumes of which were calculated based on the given content of Gd and Tb in the samples. $Gd(NO_3)_3$, $Tb(NO_3)_3$ solutions of given concentration were prepared by dissolving the corresponding oxides of Gd_2O_3, Tb_4O_7 in HNO_3 (extra-pure grade). When Tb_4O_7 was dissolved, hydrogen peroxide H_2O_2 (extra-pure grade) was also added. The resulting mixture was stirred for 3 h, and a 25%- solution of NH_4OH was introduced into the resulting pulp to pH ∼ 10. The residue was filtered off, washed with deionized water at a solid-to-liquid ratio of 1:3, dried at ∼ 150°C, and calcined at 700°C for 4 h. Then the powders were ground in an MK 1 ball chalcedony mill and calcined in a KEP14/1400P electric furnace for 4 h at ∼ 1200°C.

In fluoride Nb- and Ta--containing solutions, the content of niobium and tantalum was determined by the gravimetric method, fluoride-ions — potentiometrically on the EW ionometer -74 with F-selective electrode EWL-1M3. Fluorine in the synthesized powders was analyzed by pyrohydrolysis. Gd and Tb in filtrates and wash solutions were determined by atomic-emission spectrometry (AES-ICP) on an ICPE 9000 spectrometer, Shimadzu.

AES-ICP data showed that in filtrates and washing solutions, the concentrations of Gd ($1{-}3 \cdot 10^{-5}$ g/l), Tb ($< 1 \cdot 10^{-4}$ g/l) were trace amounts. Consequently, Gd and Tb almost completely passed from solutions of $Gd(NO_3)_3$ and $Tb(NO_3)_3$ into the hydroxide precipitate under the selected conditions. The fluorine concentration in the powders was below the sensitivity limit of the analysis method used (less than $1 \cdot 10^{-3}$%).

Elemental composition of ceramic samples $(Gd_{1-x}Tb_x)Nb_yTa_{1-y}O_4$ according to EPMA data

Sample	Planned composition	Element content (PCMA), formula units	
		Tb, x	Nb, y
NbTa0.05	$(Gd_{0.95}Tb_{0.05})Nb_{0.9}Ta_{0.1}O_4$	0.052±0.004	0.892±0.010
NbTa0.1	$(Gd_{0.9}Tb_{0.1})Nb_{0.9}Ta_{0.1}O_4$	0.097±0.003	0.908±0.010
NbTa0.15	$(Gd_{0.85}Tb_{0.15})Nb_{0.9}Ta_{0.1}O_4$	0.149±0.004	0.905±0.009
NbTa0.2	$(Gd_{0.8}Tb_{0.2})Nb_{0.9}Ta_{0.1}O_4$	0.188±0.004	0.902±0.006
Nb0.05	$(Gd_{0.95}Tb_{0.05})NbO_4$	0.049±0.002	0.999±0.004
Nb0.1	$(Gd_{0.9}Tb_{0.1})NbO_4$	0.100±0.005	0.996±0.004
Nb0.15	$(Gd_{0.85}Tb_{0.15})NbO_4$	0.133±0.028	0.996±0.002
Nb0.2	$(Gd_{0.8}Tb_{0.2})NbO_4$	0.193±0.009	1.000±0.001

Ceramic samples in the form of tablets with diameter of 5–10 cm were pressed of the resulting powder at pressure of about 3.8 kg/cm^2. Polyvinyl alcohol was used as a binder. After pressing, the tablets were hold in a KEP 14/1400P electric furnace at 1380°C for 3 h.

The elemental composition of the samples was studied by electron probe microanalysis (EPMA) on a Camebax electron probe microanalyzer equipped with four X-ray spectrometers. Rare-earth element phosphates $GdPO_4$, $TbPO_4$ and Nb and Ta metals (99.9% purity) were used as standards. The following analytical lines were used for the analysis: Gd — Lα, Tb — Lα, Ta — Mα, Nb — Lα. The oxygen content in the solid solution was calculated based on stoichiometry. The analysis was carried out in 8–12 random areas of each sample. In this case, the accelerating voltage of the electrons was equal to 20 kV, the absorbed current was $I = 5{-}10$ nA. The electron beam diameter was ∼ 5 μm.

The phase composition of the obtained samples was studied by X-ray diffraction phase analysis (XDPA) on a D2 Phaser diffractometer (Bruker, Germany) (copper tube, $\lambda = 1.5406$ Å, accelerating current and voltage — 10 mA and 30 kV) equipped with a PSD-detector. The phase composition was interpreted using the Eva software package (Bruker) based on the ICDD database (PDF 2, relies 2014).

Photoluminescence spectra were obtained using a Fluorolog-3 „Horiba“ spectrofluorometer at excitation wavelength of 260 nm. Also, the luminescent properties of the materials were studied by the method of local cathodoluminescence (CL) on the same Camebax setup, which was used for EPMA. Such a combination made it possible to study the luminescence and elemental composition of the same sample microvolume. The accelerating voltage when obtaining CL- spectra and attenuation times (τ) of luminescence intensity was 20 kV, absorbed current —

10 nA, electron probe diameter — 2 μm. The kinetics of CL bands was measured in the mode of electron beam deflection.

When performing studies on a Camebax electron probe microanalyzer, all samples were fixed in measuring cassettes using Rose alloy. To ensure that the charge drains from the surface of the material during electron beam irradiation, a carbon film was additionally deposited on the surface of the samples on a JEE-4C universal vacuum post.

Results and discussion

Elemental and phase composition

EPMA showed that the measured average elemental composition of the samples corresponded to the given one for almost all samples within the error of the method used (table). However, for the Nb0.15 sample, the relative deviation of the Tb content in random areas of the sample exceeds the method error (10% for low concentrations) and amounts to 21%. This indicates significant heterogeneity of the activator distribution for this sample.

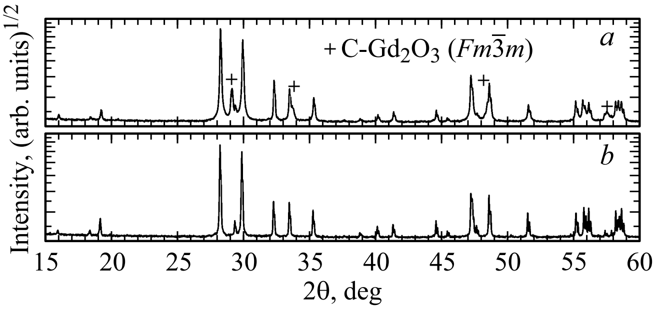

Figure 1. Diffractograms of ceramic samples ($\lambda = 1.5406$ Å, accelerating current and voltage — 10 mA and 30 kV): (*a*) sample $(Gd_{0.95}Tb_{0.05})Nb_{0.9}Ta_{0.1}O_4$ (NbTa0.05); (*b*) sample $(Gd_{0.95}Tb_{0.05})NbO_4$ (Nb0.05).

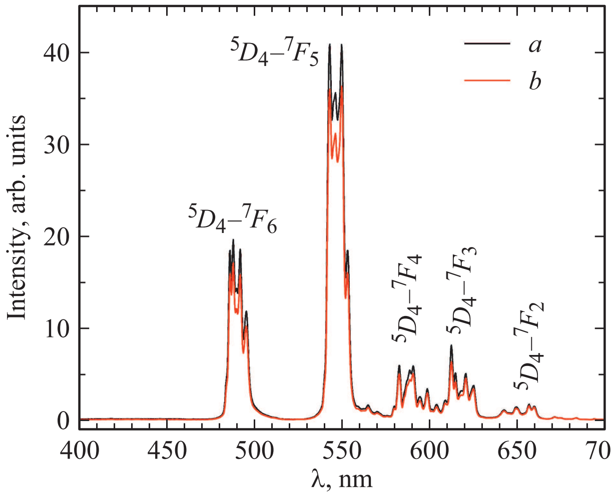

Figure 2. Photoluminescence spectra of ceramics: (*a*) sample $(Gd_{0.95}Tb_{0.05})Nb_{0.9}Ta_{0.1}O_4$ (NbTa0.05); (*b*) sample $(Gd_{0.95}Tb_{0.05})NbO_4$ (Nb0.05).

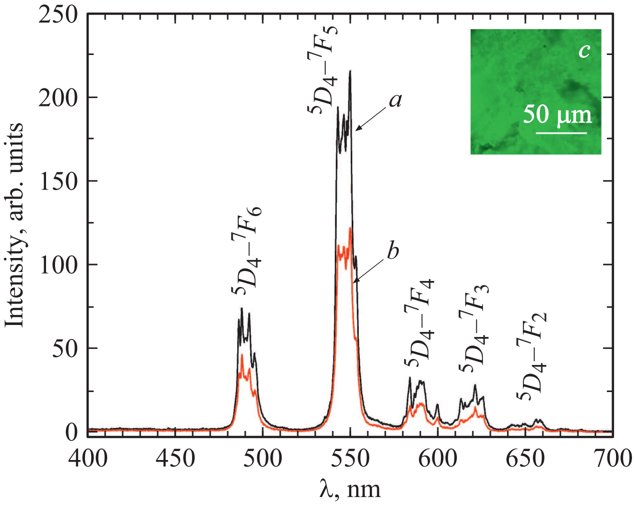

Figure 3. CL spectra of ceramics: (*a*) sample $(Gd_{0.95}Tb_{0.05})Nb_{0.9}Ta_{0.1}O_4$ (NbTa0.05); (*b*) sample $(Gd_{0.95}Tb_{0.05})NbO_4$ (Nb0.05); (*c*) KL- Nb0.05 sample image.

Gadolinium niobates can have two crystal modifications: tetragonal T (at high temperatures) and low-temperature monoclinic M [1,5]. Gadolinium tantalates (besides the two mentioned above) have an additional modification — a monoclinic polytype M' with a lattice parameter *b* reduced by half (relative to the polytype M) [5]. This modification is implemented at lower temperatures than the M modification [13]. According to the results of XDPA, all obtained samples are $GdNbO_4$ of monoclinic syngony with space group $I2/a$ (M-polytype, PDF 01-075 -5932). An insignificant amount of Gd_2O_3 impurities was found in the NbTa0.05, NbTa0.2, and Nb0.1 samples. The maximum relative content of gadolinium oxide does not exceed 5% for the NbTa0.05 sample and 2–3% for the NbTa0.2, Nb0.1 samples. Terbium-based impurity phases were not detected. Examples of the obtained diffraction patterns are shown in Fig. 1.

Luminescent properties

For two samples with tantalum in the composition $(Gd_{0.95}Tb_{0.05})Nb_{0.9}Ta_{0.1}O_4$ (NbTa0.05) and without tantalum $(Gd_{0.95}Tb_{0.05})NbO_4$ (Nb0.05), photoluminescence spectra were obtained (region 1 × 5 mm, Fig. 2). The figure shows that the shape of the luminescence spectra is identical for both samples.

For all the obtained materials, CL spectra were also obtained. This method was distinguished by greater locality (electron beam diameter ~ 2 μm). Examples of the spectra obtained for NbTa0.05 and Nb0.05 samples are shown in Fig. 3, *a, b*. The same radiative bands can be observed on them as in the case of photoexcitation. The interpretation of radiative transitions in the photoluminescence

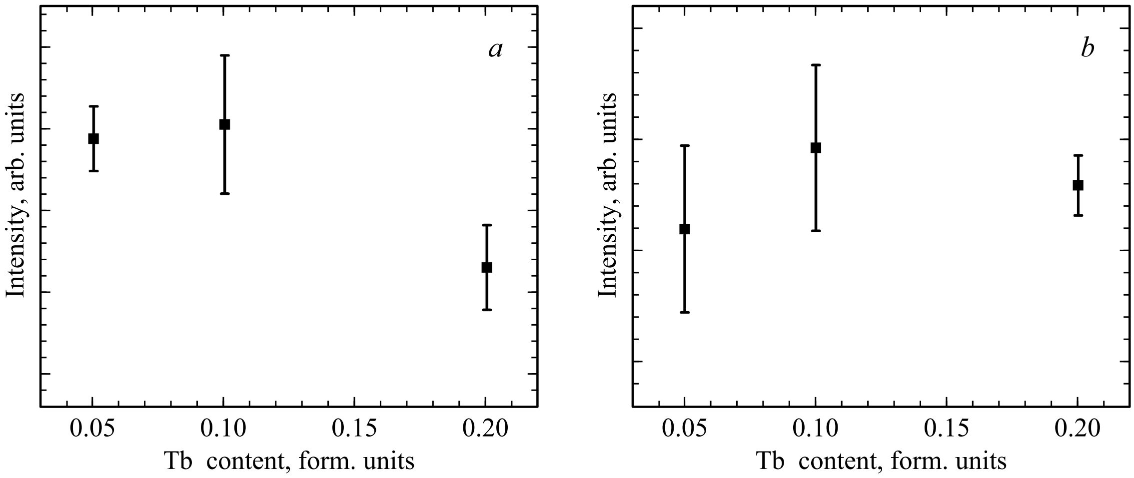

Figure 4. Concentration dependences of CL intensity: (*a*) series of samples $(Gd_{1-x}Tb_x)Nb_{0.9}Ta_{0.1}O_4$ (NbTa0.05−NbTa0.2); (*b*) series of samples $(Gd_{1-x}Tb_x)NbO_4$ (Nb0.05−Nb0.2).

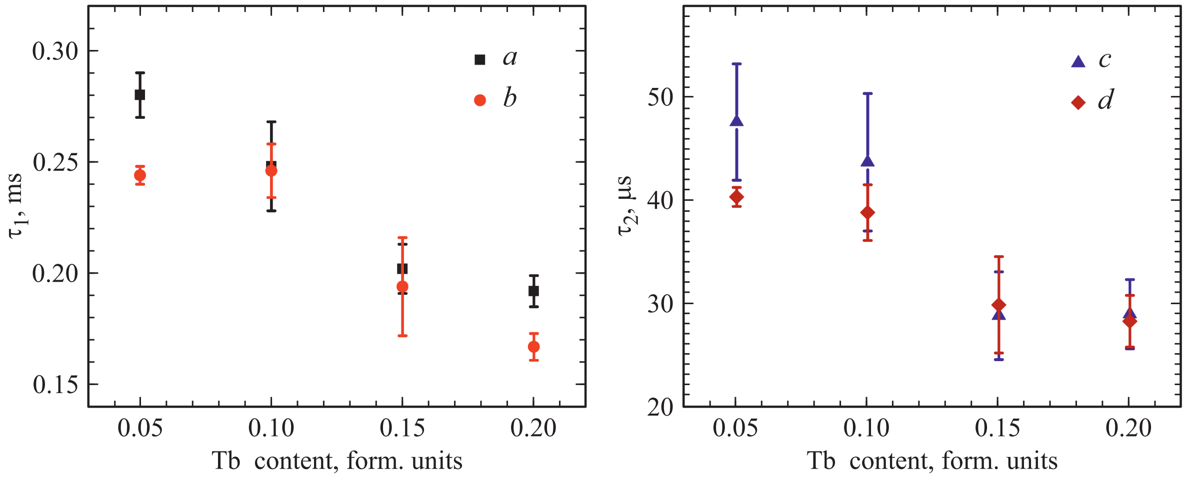

Figure 5. Concentration dependences of CL attenuation times: (*a, c*) series of samples $(Gd_{1-x}Tb_x)Nb_{0.9}Ta_{0.1}O_4$ (NbTa0.05−NbTa0.2); (*b, d*) series of samples $(Gd_{1-x}Tb_x)NbO_4$ (Nb0.05− Nb0.2).

and CL spectra was carried out according to the literature data [3,17,18]. On the graphs, one can observe bands of transitions from the $^5D_4$ level to the ^7F_j levels ($j = 2$−6). No transitions from the $^5D_3$ level are observed. Most likely, this is due to quenching of radiation from this level as a result of excitation cross-relaxation to the $^5D_4$ [17,19] level. The obtained CL-images showed the heterogeneity of the luminescence intensity in the synthesized samples (example of CL-images — Fig. 3, *c*). Most likely, this is due to the features of the surfaces of the studied ceramics, since EPMA did not show a significant heterogeneity of the activator distribution for all samples, except for Nb0.15. Due to such heterogeneity, it was not possible to reliably determine which of the compositions (NbTa0.05 or Nb0.05) has a brighter luminescence.

For two series of samples ($(Gd_{1-x}Tb_x)Nb_{0.9}Ta_{0.1}O_4$ and $(Gd_{1-x}Tb_x)NbO_4$) concentration dependences of the luminescence intensity of the brightest transition $^5D_4$−$^7F_5$ (Fig. 4) were obtained. At the same time, the intensities of samples with terbium content of 0.15 form. units are not shown in Fig. 4 due to the fact that they turned out to be significantly lower than expected. The surface color of these ceramic samples is significantly darker than that of the other series. However, EPMA and XDPA did not reveal deviations that could lead to such a change in appearance. The reason for this difference has not yet been established.

When certain concentration of the activator in the matrix is reached, the luminescence yield should begin to decrease. This occurs as a result of energy transfer between neighboring activator ions, which is accompanied by an increase in the probability of nonradiative recombination. Such a phenomenon is called concentration quenching [20]. Due to the significant heterogeneity of the luminescence in the studied ceramics, it is difficult to draw a definite conclusion about the presence of quenching based on Fig. 4. However, one can notice a decrease in the luminescence intensity for samples with a Tb^{3+} content of 0.2 form. units. To refine the concentration of the activator at which quenching begins, the concentration dependences of the CL attenuation times for the same transition $^5D_4-^7F_5$ were obtained. In this case, the attenuation times are presented for all samples of both series. All luminescence attenuation curves after the sample was irradiated with an electron beam contained two components. The presence of two attenuation times can be explained by the influence of the surface of the grains that make up the ceramic [21]. The concentration dependences for each of the components are given in Fig. 5, *a, b, c, d*. It can be seen from the presented curves that the attenuation times decrease with increase in activator content. This indicates the presence of concentration quenching. In this case, the curves for the series $(Gd_{1-x}Tb_x)NbO_4$ are flatter. Based on the data obtained, it can be concluded that for samples with the presence of tantalum in the composition, quenching occurs earlier than for pure gadolinium niobate. However, to determine the exact composition at which the phenomenon of concentration quenching begins, it is necessary to synthesize samples with a lower content of the activator Tb^{3+}.

Conclusions

Terbium-activated gadolinium tantalo-niobates $((Gd_{1-x}Tb_x)Nb_yTa_{1-y}O_4$, where $x = 0.05-0.2$; $y = 0.9$, 1) were synthesized for the first time. The liquid-phase method was used for the synthesis.

The resulting ceramic samples were studied by electron probe microanalysis, X-ray diffraction phase analysis, photoluminescence, and CL methods. Almost all synthesized materials had an average elemental composition corresponding to the planned one. All the studied samples had the main phase M $GdNbO_4$. The relative content of impurity phases did not exceed 2−5%.

The resulting photoluminescence and CL spectra show bands of transitions from the $^5D_4$ level to the ^7F_j levels $(j = 2-6)$. It has been established that concentration quenching for a series with tantalum in the composition $((Gd_{1-x}Tb_x)Nb_{0.9}Ta_{0.1}O_4)$ occurs earlier than for the series without tantalum $((Gd_{1-x}Tb_x)NbO_4)$. To accurately determine the concentration of the activator at which the decrease in the luminescence intensity begins, it is necessary to synthesize gadolinium tantalum-niobates with lower content of terbium.

The resulting materials exhibit bright green luminescence and are promising for use as scintillators.

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Conflict of interest

The authors declare that they have no conflict of interest.

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