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New, dense, and fast scintillators based on rare-earth tantalo-niobates

O.V. Voloshyna [a,*], I.A. Boiaryntseva [a], V.N. Baumer [b], A.I. Ivanov [a], M.V. Korjik [c], O.Ts. Sidletskiy [a]

[a] *Institute for Scintillation Materials NAS of Ukraine, 60, Lenin Av., 61001 Kharkiv, Ukraine*
[b] *SSI "Institute for Single Crystals", NAS of Ukraine, 60, Lenin Av., 61001 Kharkiv, Ukraine*
[c] *Institute for Nuclear Problems, 11, Bobruiskaya Str. 11, 220030 Minsk, Belarus*

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ABSTRACT

Samples of undoped yttrium and gadolinium tantalo-niobates with common formulae RE(Nb_xTa_{1-x})O_4, where RE=Y or Gd and x=0–1, have been obtained by solid-state reaction. Systematic study of structural, luminescent, and scintillation properties of these compounds was carried out. Lattice parameters and space groups of the mixed compounds were identified. UV- and X-ray luminescence spectra, as well as relative light outputs and scintillation decay times are measured. Gadolinium tantalo-niobate with the formulae $GdNb_{0.2}Ta_{0.8}O_4$ showed the light output around 13 times larger than $PbWO_4$ and fast decay with time constant 12 ns without additional slow component. Gadolinium tantalo-niobates may be considered as promising materials for high energy physics due to extremely high density, substantial light output, and fast decay.

1. Introduction

High density and effective charge Z_{eff} are crucial parameters of scintillators in most of applications, in particular, in high energy physics. These parameters determine the stopping power of a material and, as the issue, reduction of the detector volume needed. The highest Z_{eff} in scintillators can be achieved in Pb, Bi, Nb, Ta or lanthanide-containing compounds. The successful examples of dense scintillator development comprise $PbWO_4$ [1–3], $Bi_4Ge_3O_{12}$ [4–6], Gd_2SiO_5:Ce [7], Lu_2SiO_5:Ce [8], $Lu_{2x}Y_{2-2x}SiO_5$:Ce [9]. Lead tungstate is widely used in precise electromagnetic calorimetry in high energy physics experiments, for example, in the electromagnetic calorimeter of CMS Collaboration detector at CERN [10]. LYSO:Ce and GSO:Ce scintillators are candidates for usage in calorimeters for registration of electron-muon conversion—the μ2e Experiment in Fermilab [11] and COMET in KEK [12]. LSO:Ce and LYSO:Ce are also materials of choice for PET scanners in medical applications [13].

Compounds with the general formula $REAO_4$, where RE—rare earth element and A—transition metal-element of 5th group (V, Nb or Ta) of Periodic table, are considered as efficient luminescence materials with high density for registration of X- and γ-rays [14–16]. Rare-earth doped yttrium tantalate-based compounds [17,18] attract attention due to promising properties for utilizing in optoelectronics and X-ray intensifying screens for electronic detector systems. Less attention is paid to the undoped $REAO_4$ compounds, because rare-earth vanadates and niobates possess slow luminescence decay making impossible to utilize them in applications where fast signal readout is necessary. Tantalates demonstrate the weakest luminescence relatively to vanadates and niobates [14,16,19]. Meanwhile, the density of up to 9.75 g/cm^3 [20] may be achieved in rare-earth tantalates, which is the highest value among the known scintillator compounds.

Recently it was shown that significant improvement of the light yield can be obtained in mixed crystals compared to their constituents [21]. In particular, excellent light yield of up to 56,500 ph/MeV was detected with gadolinium gallium–aluminum garnet mixed crystal [22], light yield of 34,000 ph/MeV was achieved in $Lu_{2-2x}Gd_{2x}SiO_5$:Ce [23]. Possible mechanism of this phenomenon is discussed elsewhere [24]. It is to clarified completely yet, however mixed crystals engineering, for sure, can be a powerful tool to improve the parameters of scintillators. Recently, a fast luminescence with the main decay component of 72.6 ns was reported in $GdTaO_4$ crystal [25]. However, it is still much slower than that of $PbWO_4$, where around 95% of scintillation corresponds to a fast component with decay constants less than 20 ns. The light yield of $GdTaO_4$ is low and was evaluated to be about 3 times higher than that of $PbWO_4$ [25]. Therefore, search for new tantalo-niobate compositions combining reasonable light yield and fast luminescence decay with low contribution of slow components is a topic of interest.

To the best of our knowledge, the structure of gadolinium tantalo-niobates was not studied before. Optical and scintillation

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[*] Corresponding author. Tel.: +380573410442; fax: +380573404474.
E-mail address: lvoloshina@isma.kharkov.ua (O.V. Voloshyna).

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properties of yttrium and gadolinium tantalo-niobates were not determined as well. This study is aimed to evaluate the crystallographic parameters, as well as luminescent and scintillation properties of yttrium and gadolinium tantalo-niobate compounds depending on the Ta/Nb ratio in the hosts.

2. Experimental

2.1. Sample preparation

Tantalate-based samples were prepared by the solid-state reaction. Y_2O_3, Gd_2O_3 (Stanford Materials Co, USA) and Ta_2O_5, Nb_2O_5 (Lanhit, Russia) with the purity not less than 4 N were used as the starting materials. Starting oxides were pre-annealed to remove absorbed moisture and CO_2, weighted in composition with the molar ratio of components RE_2O_3: Z=1:1, where RE=Y or Gd and Z=Ta_2O_5, Nb_2O_5 or mixture of $x\ Nb_2O_5+(1-x)\ Ta_2O_5$, $x=0$–1 and afterwards mixed in agate mortar with addition of absolute ethanol (C_2H_5OH). Raw materials were pressed into pellets with the diameter 10 mm and thickness 2 mm, then the pellets were calcined at 1400 °C for 30 h in air atmosphere.

Pellets of tantalo-niobates after solid-state reaction were ground in agate mortar for XRD study. Luminescent and scintillation properties were explored using pellets polished by the same procedure to maintain the same surface roughness, and, as a sequence, the same light collection conditions from the sample surface.

2.2. Determination of cell parameters

XRD studies of tantalo-niobate samples structure were carried out using an automated powder Siemens D 500 diffractometer (Bragg–Brentano geometry, 2θ range 5° to 125°, step-scanning mode, $\Delta 2\theta=0.02°$, counting time of 10 s). Rietveld analysis [26] of samples was performed with a FullProf&WinPLOTR program package [27] using crystal structure data given in [28–30].

2.3. Determination of optical and scintillation parameters

Emission spectra in the 230–800 nm range at photo excitation were determined using a combined fluorescent lifetime and steady-state spectrometer FLS 920 (Edinburgh Instruments). Xe lamp was used for steady-state measurements, and nanosecond hydrogen operated flashlamp was used for decay time measurements. Photoluminescence spectra were corrected for the spectral sensitivity of the detection system.

X-ray luminescence spectra were measured with a KSVU-23 spectrometer. X-ray emitter ($E=40$ kV, $I_a=25$ μA, Cu anode) was used for excitation. Measurements of light output in the "current mode" were carried out using an IRI X-ray source ($E=100$ kV, $I_a=1$ mA, W anode). Block of registration at light output measurements consists on platform for mounting of studied scintillator and FD-288 PMT connected to a V7-35 voltmeter. Scintillation decay times under X-rays were measured using a RIGOL DS1302CA oscilloscope at excitation by a MIRA-2D X-ray emitter with $U=200$ kV, $I_a=5$ mA, and the 10 ns impulse duration. PMT FEU35A with CsSb photocathode was used as the photo receiver. Procedures of scintillation parameters measurements are described in more detail in our previous work [14]. All the measurements were carried out at 300 K.

3. Results and discussion

3.1. Structure of mixed tantalo-niobates

The Goldshmidt's rule postulates the formation of the stable solid solution between the compounds with the difference in the ionic radii between competing atoms of not more than 15%. At that point of view, tantalo-niobate mixed crystals comprise a unique situation where the ionic radii of both atoms in the oxidation state +5 and six-fold coordination are the same and equal to 0.64 Å [31]. Existence of the stable solid solution for the full range of Nb concentrations in $(Nb_xTa_{1-x})_2O_5$ at $x=0$–1 was identified [32,33]. As a sequence, one can expect a formation of the mixed crystal in the plane cross-section of the ternary system RE_2O_3–Ta_2O_5–Nb_2O_5 providing total molar ratio of RE_2O_3: $[x\ Ta_2O_3+(1-x)\ Nb_2O_5]=1:1$, where $x=0$–1. However, continuous series of solid solutions in all the concentration range is observed in $GdTa_{1-x}Nb_xO_4$ only (Table 1). On the contrary, the structure transition from monoclinic P_1 2/a to monoclinic I 2/a symmetry occurs in the yttrium system between $x=0$ and 0.2. Cell parameters of mixed compounds, as well as their calculated densities are depicted in Table 1. The densities are calculated basing on the data on densities of rare-earth orthotantalates and orthoniobates from [20] assuming that the densities of mixed compounds correspond to the Vegard's law [34].

The cell parameters increase linearly with increasing of the Nb content in the host (see Table 2) due to longer distances between A^{5+} and oxygen ions in Nb-based host [29,30]. This phenomenon, probably, is the issue of the different electronegativities of Ta (1.5, Pauling scale) and Nb (1.6, Pauling scale), and, as a sequence, the different partial charges on the Ta^{5+}, Nb^{5+} and O^{2-} ions in compounds with the covalent bond. It is known that ionic radius

Table 1
Cell parameters of the yttrium and gadolinium orthotantalates, orthoniobates and tantalo-niobates.

Nb content, x	Space group	a (Å)	b (Å)	c (Å)	β (degree)	Density (g/cm^3), calculated
			$Y(Ta_{1-x}Nb_x)O_4$			
0	P_1 2/a	5.299	5.456	5.111	96.412	7.56
0.2	I 2/a	5.322	10.935	5.057	95.386	7.16
0.4	I 2/a	5.317	10.938	5.059	95.232	6.75
0.6	I 2/a	5.314	10.943	5.065	95.045	6.34
0.8	I 2/a	5.306	10.946	5.069	94.808	5.94
1.0	I 2/a	5.299	10.949	5.073	94.561	5.53
			$Gd(Ta_{1-x}Nb_x)O_4$			
0	I 2/a	5.405	11.060	5.081	95.620	8.76
0.2	I 2/a	5.401	11.072	5.087	95.460	8.37
0.4	I 2/a	5.395	11.080	5.092	95.276	7.98
0.6	I 2/a	5.387	11.085	5.097	95.042	7.58
0.8	I 2/a	5.379	11.090	5.102	94.812	7.19
1.0	I 2/a	5.372	11.095	5.107	94.563	6.80

Table 2
Interatomic distances between the A^{5+} and O^{2-} ions in the orthoniobates and orthotantalates.

Distance	$GdNbO_4$	$YNbO_4$	$GdTaO_4$	$YTaO_4$
Nb–O(1)$_a$[O(1)$_b$]	1.862(3)	1.824(3)	–	–
Nb–O(2)$_a$[O(2)$_b$]	1.916(3)	1.917(2)	–	–
Nb–O(2)$_c$[O(2)$_d$]	2.441(3)	2.415(3)	–	–
(Nb–O) average	2.073(3)	2.052	–	–
Ta–O(1)$_a$[O(1)$_b$]	–	–	1.993(5)	1.974(6)
Ta–O(1)$_a$[O(1)$_b$]	–	–	2.108(5)	2.216(6)
Ta–O(2)$_c$[O(2)$_d$]	–	–	1.872(5)	1.864(6)
(Ta–O) average	–	–	2.024	2.018