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Nonlinear behavior of structural and luminescent properties in $Gd(Nb_xTa_{1-x})O_4$ mixed crystals

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ABSTRACT

Ceramic samples of gadolinium tantalo-niobate mixed crystals were obtained by the solid-state technique. The dependence of luminescence properties on the Nb/Ta ratio in the $Gd(Nb_xTa_{1-x})O_4$ system is studied in the 5–450 K temperature range, including thermostimulated luminescence curves in the series of solid solutions. The relation of nonlinear behavior of light output with x variation to non-homogeneous distribution of Nb and Ta in solid solutions is discussed.

1. Introduction

Currently the fast and heavy crystals are needed for the application in scintillation detectors [1]. Scintillators with activator emission are commonly used for such purposes. However, crystals with intrinsic emission are preferable in case of cryogenic scintillators when activator emission becomes inefficient due to the self-trapping of charge carriers by the host lattice at low temperature [2,3]. $REAO_4$ compounds (A = Ta or Nb) demonstrate intrinsic luminescence attributed to the emission of regular TaO_6 - and NbO_6 – groups and defect groups NbO_5V_O and TaO_5V_O (V_O – oxygen vacancy) [4–7]. The brightest luminescence was observed in the rare earth niobates [4]. At the same time, rare-earth tantalates demonstrate an extremely high density and stopping power [8]. Engineering of mixed compositions by Nb^{5+}/Ta^{5+} substitution can be a tool to enhance the light yield and other scintillation parameters by analogy with many other mixed systems studied recently [9–16]. It was shown that the tendency to light yield increase in mixed crystals is linked to the spatial distribution of substituted atoms in solid solutions which, in turn, determines their electronic properties. Basing on luminescence properties study it was suggested that spatial inhomogeneities of electronic structure affect the dynamics of relaxation, recombination, and localization of free carriers [9,10,12]. This approach was confirmed by the dependence of light yield improvement in mixed crystals on ionic radii difference between the substituted atoms [17]. Meanwhile, the improvement of charge carriers transport efficiency to activator and a huge light yield increase was linked to enveloping of the electron trap levels in the conduction band in some mixed crystals [18–21].

Light output and decay times of the tantalo-niobates $[RE(Nb_xTa_{1-x})O_4]$ strongly depends on the Ta/Nb ratio [22]. Light output of $Gd(Ta_{1-x}Nb_x)O_4$ at room temperature shows about gradual increase with Nb content. The fast decay component with the τ varied within 5–93 ns range is accompanied by the slow component for all compositions except $Gd(Ta_{0.8}Nb_{0.2})O_4$. Recently, single crystals with the latter composition were successfully grown by the Czochralski technique [23]. In this scintillator the high density of 8.37 g/cm^3 is combined with the light output of 1400 ph/

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MeV and very fast luminescence with the main decay time of 17 ns.

The present study focuses on structural and luminescence properties of $Gd(Ta_{1-x}Nb_x)O_4$ (x = 0 ÷ 1), including thermo-stimulated luminescence (TSL) curves analysis. We also discuss the evidences of clusterization in these solid solutions basing on dependences of various physical properties on the Ta/Nb ratio.

2. Experimental

2.1. Raw materials

Ceramic samples of gadolinium tantalate-based compounds with varying Nb content from 0 to 100 at.% were obtained by the solid-state synthesis (details are described in Ref. [22]). Gd_2O_3 (Stanford Materials Co, USA) and Ta_2O_5, Nb_2O_5 (Lanhit, Russia) with purity not less than 4N were used as starting materials. XRD data on the obtained samples indicate that all the $Gd(Nb_xTa_{1-x})O_4$ samples crystallize in the M-fergusonite structure (space group I 2/a) with the main phase content of 95–97 wt% [22]. After solid-state synthesis the pellets were prepared for the study of luminescent and scintillation properties by polishing of their surfaces to the identical surface roughness providing the same light collection conditions from all of the samples.

2.2. Characterization techniques

The luminescence spectra under excitation with synchrotron radiation (SR) with excitation energy 22 eV have been obtained at the branch-line FINEST at MAX-lab, Lund [24]. The spectra were measured using ARC Spectra Pro 300i monochromator equipped with Hamamatsu H6240-01 photon counting head in the temperature range 5–300 K. TSL curves were studied in the temperature range T = 100–550 K. Samples were mounted into LINKAM THMS600 Stage. The spectra were registered using a Shamrock 500i spectrograph equipped with a Newton EMCCD DU970P. The heating rate at TSL measurements was 10 K/min.

The luminescence excitation spectra were measured at 300 K in the wavelength range 200–350 nm using the deuterium Heraeus D 200 VUV lamp as an excitation source. The McPherson Model 234/302 primary monochromator was used for the selection of excitation wavelength. The luminescence was registered using the Shamrock 303i (Andor Technology) monochromator equipped with the Hamamatsu H8259 photon counting head.

3. Experimental results

3.1. Cell parameters

Deviations of lattice constants from the Vegard's law were noticed previously in many mixed crystals, e.g. in MgO-FeO, MgO-$LiFeO_2$ [25], and CdF_2-PbF_2 systems [26], and attributed to the formation of inhomogeneities (clusters) enriched with one of substituted atoms. In $Gd(Nb_xTa_{1-x})O_4$ the *b* cell parameter and the elementary cell volume determined recently in Ref. [22] demonstrate similar positive deviations at x = 0.2–0.6 (Fig. 1).

3.2. Luminescence properties

The luminescence spectra of $Gd(Nb_xTa_{1-x})O_4$ at T = 300 K are presented in Fig. 2a. The excitation energy of SR was 22 eV providing interband electron transitions. The excitation energy is high enough to model the processes which takes place in a scintillator at the final stages of energy relaxation including the photon multiplication, thermalization of hot charge carriers and their migration to the emission centers. The photon multiplication

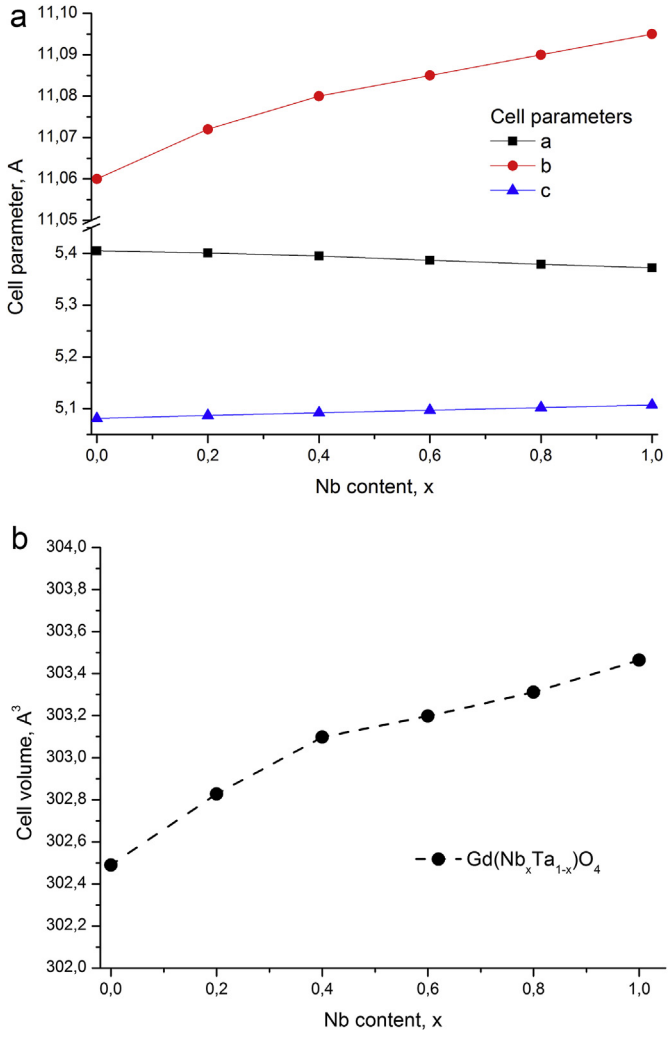

Fig. 1. Dependence of the cell parameters (a) and cell volume (b) on the x value for $Gd(Ta_{1-x}Nb_x)O_4$.

process starts at $E_{ex} \geq 2E_g$. According to [27] the band gap energies for gadolinium tantalate and niobate are 5.4 eV and 4.6 eV, respectively. Therefore, the excitation energy exceeds the bandgap values of the studied samples by the factor of 4.1–4.8. At $x \neq 0$ all the samples demonstrate a broad emission band with the maximum around 450 nm. It was shown previously [28] that emission in rare earth tantalo-niobates possesses the complex structure and consists of the short-wavelength band peaked at 415 nm and ascribed to the exciton-like emission at regular oxy-anion complexes NbO_6, and the long-wavelength band peaked at 460 nm, which is connected with the point defects, in particular, oxygen vacancies (NbO_5V_O-group). Consequently, the $Gd(Nb_xTa_{1-x})O_4$ emission observed in this work at room temperature can be ascribed to the defect-related emission.

The intrinsic emission is not manifested, probably, due to the thermal quenching, or due to efficient transfer from regular to defect states [4]. The broad but weak emission band in $GdTaO_4$ (Fig. 2a, curve 1) is red-shifted and linked to TaO_5V_O-group emission [28]. The several sharp peaks at 380, 420, 440, 490, 550, 590 and 610 nm observed for the latter are related to emission of Eu^{3+} and Tb^{3+} impurities. The peak at 310 nm linked with the emission of the cell-forming Gd^{3+} ion and is most pronounced for the $GdTaO_4$. Less intensity of this band for Nb-containing samples