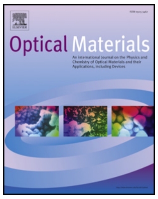
Optical Materials 80 (2018) 247–252

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Composition effect in luminescence properties of $Y(Nb_xTa_{1-x})O_4$ mixed crystals

D. Spassky[a,*], A. Vasil'ev[a], S. Vielhauer[b], O. Sidletskiy[c], O. Voloshyna[c], A. Belsky[d]

[a] Skobeltsyn Institute of Nuclear Physics, Moscow State University, Moscow, Russia
[b] Institute of Physics, University of Tartu, W. Ostwaldi Str.1, 50411, Tartu, Estonia
[c] Institute for Scintillation Materials NAS of Ukraine, Kharkiv, Ukraine
[d] Institute of Light and Matter, CNRS, University Lyon1, France

ARTICLE INFO

Keywords:
Yttrium tantalate
Yttrium niobate
Mixed crystals
Luminescence
Energy transfer
Thermalization length

ABSTRACT

The luminescence properties of $Y(Nb_xTa_{1-x})O_4$ mixed crystals were studied. Local structure modifications arise due to the inhomogeneous distribution of the substitutional ions in the mixed crystal and can be traced using the luminescence spectroscopy. In particular, it is shown that the intensity of exciton emission under interband VUV excitation increases for intermediate values of **x** with the maximum at **x** = 0.4 relatively to the intensity observed in the constituents of the mixed crystals - $YTaO_4$ and $YNbO_4$. From the luminescence excitation spectra it follows that the probability of exciton creation from the separated e-h pairs increases for intermediate values of **x** as well. Using numerical simulation it is shown that the effect is connected with the variation of the thermalization length of hot electrons and holes, which is minimal at **x** = 0.4.

1. Introduction

Scintillators with efficient conversion of high-energy radiation into luminescence are needed for application in new experiments in fundamental physics as well as in the medical imaging, new security control systems, etc. Compounds with NbO_4 complex are characterized by the bright intrinsic luminescence in a wide temperature region, whereas the highest density can be achieved in compounds with TaO_4 complex – up to 9.34 g/cm^3 for $LuTaO_4$ [1]. In particular, the luminescence and scintillation properties of $YNbO_4$ and $YTaO_4$ undoped as well as doped with rare-earth elements have been extensively studied [2–6]. Mixed crystals allow tuning the optical and luminescence properties and obtaining a better combination of properties than for the constituents of mixed crystals. It can be expected that $Y(Nb_xTa_{1-x})O_4$ substitutional solid solutions (or mixed crystals) will combine the advantageous properties of both compounds. Usually the properties of the substitutional solid solutions change gradually with composition and follow Vegard's law [7,8]. However, non-linear dependence of light output on the relative concentration of substituted ions is a distinctive feature of many mixed crystals. The enhancement of light output in the mixed crystals has been observed in Refs. [9–14] and makes it attractive for their application in scintillators and X-ray phosphors. The origin of the effect is generally ascribed to the limitation of the free mean path of charge carries at the stage of their thermalization and migration to the emission centers [15,16]. In particular, it was shown that the dependence of thermalization length of charge carriers on the composition of the mixed crystal determines the light output in $Zn_xMg_{1-x}WO_4$ [14]. Here we present the study of the luminescence properties of $Y(Nb_xTa_{1-x})O_4$ mixed crystals. Special attention will be paid to the origin of the light output modification with the **x** value of $Y(Nb_xTa_{1-x})O_4$.

2. Experimental details

Samples of $Y(Ta_{1-x}Nb_x)O_4$ with x = 0, 0.2, 0.4, 0.6, 0.8, 1 have been synthesized by solid-state reaction. Y_2O_3 (Stanford Materials Co, USA) and Ta_2O_5, Nb_2O_5 (Lanhit, Russia) with purity not less than 4 N were used as starting materials. Content of the main phase in the samples after solid-state synthesis was determined about 95–97%. According to XRD data, the M fergusonite crystal structure is formed for all studied crystals except $YTaO_4$. In this structural type the octahedra are connected by the edges and form chains along the a-axis. $YTaO_4$ is crystallized in the M′ fergusonite structural type. The structure is characterized by cube – like eight coordinated Y polyhedral while Ta atoms are located in the distorted octahedrons.

The measurements of luminescence were performed under UV, VUV and X-ray excitation. Experiments with excitation in VUV energy region were performed using synchrotron radiation at the branch-line FINEST at MAX-lab, Lund [17]. The spectra were measured with an ARC

---

[*] Corresponding author.
E-mail address: deris2002@mail.ru (D. Spassky).

https://doi.org/10.1016/j.optmat.2018.05.019
Received 29 December 2017; Received in revised form 5 May 2018; Accepted 7 May 2018

Spectra Pro 300i monochromator equipped with Hamamatsu H6240-01 photon counting head in the temperature range 5–300 K. Measurements of luminescence spectra and TSL glow curves were carried out under X-ray irradiation in the temperature region 80–470 K. X-ray irradiation was performed using an X-ray tube (W-anode, 20 mA and 30 kV) run by an INEL XRG 3000 generator. The spectra were registered using a Shamrock 500i spectrograph equipped with Newton EMCCD DU970P. TSL curves were recorded after X-ray irradiation of samples for 10 min at T = 80 K. Samples were mounted into LINKAM THMS600 Stage.

The luminescence excitation spectra were measured using a specially designed VUV setup. A 200-W deuterium discharge lamp Heraeus D200 VUV was used as an excitation source in the energy range 3.5–9 eV. The excitation wavelength was selected using a McPherson Model 234/302 monochromator. Samples were mounted into an ARS closed cycle helium vacuum cryostat. The luminescence signal was registered using a Shamrock 303i-B spectrograph equipped with a Hamamatsu photon counting head H6240-01. The excitation spectra were corrected using sodium salicylate.

3. Results and discussion

3.1. The luminescence of $\mathrm{Y(Nb_xTa_{1-x})O_4}$

Three types of emission bands have been observed in $\mathrm{Y(Nb_xTa_{1-x})O_4}$ (Fig. 1). The intrinsic emission observed in $\mathrm{Y(Nb_xTa_{1-x})O_4}$ is connected with excitons, self-trapped at $\mathrm{NbO_6}$ (**x** ≠ 0) or $\mathrm{TaO_6}$ (x = 0) groups [18–20]. The emission band peaking at 350 nm with τ_{dec} = 2.7 μs (T = 300 K) is observed only for crystals with **x** = 0 and is ascribed to self-trapped excitons (STE) at $\mathrm{TaO_6}$. When **x** ≥ 0.2, a band at 420 nm is observed under interband excitation, which is ascribed to STE at $\mathrm{NbO_6}$. The decay time of the emission is gradually decreasing from 7.5 (**x** = 0.2) to 3.5 μs (**x** = 1) Additional band at 460 nm with τ_{dec} ~ 1.5 μ also appears under interband and intraband excitations, which is ascribed to $\mathrm{NbO_5V_O}$ defect complexes.

The temperature dependence of the STE emission under X-ray excitation is presented in Fig. 2. The emission of $\mathrm{YNbO_4}$ and especially of $\mathrm{YTaO_4}$ is partially quenched at 300 K, and will result in instability of their scintillation properties with changing temperatures. The threshold of temperature quenching shifts to high temperatures with the decrease of **x**. Therefore, $\mathrm{Y(Nb_xTa_{1-x})O_4}$ mixed crystals are characterized by stable luminescence at 300 K that makes it more suitable for applications.

The position of the luminescence bands negligibly depends on the **x**. However, the modification of $\mathrm{Y(Nb_xTa_{1-x})O_4}$ band structure with **x** is manifested in luminescence excitation spectra and TSL curves. The bandgap of $\mathrm{YTaO_4}$ (5.1 eV) is larger by 0.42 eV than that of $\mathrm{YNbO_4}$ (4.68 eV) [21,22]. According to calculations of the band structure, the substitutional ions form the lower part of the conduction band [22,23]. Therefore, fluctuations of the energy position of the bottom conduction band will occur due to the inhomogeneous distribution of the substitutional ions in the mixed crystal. One can suppose that the bandgap energy will change linearly with **x** following Vegard's similarly to the change of the crystal lattice constants [24].

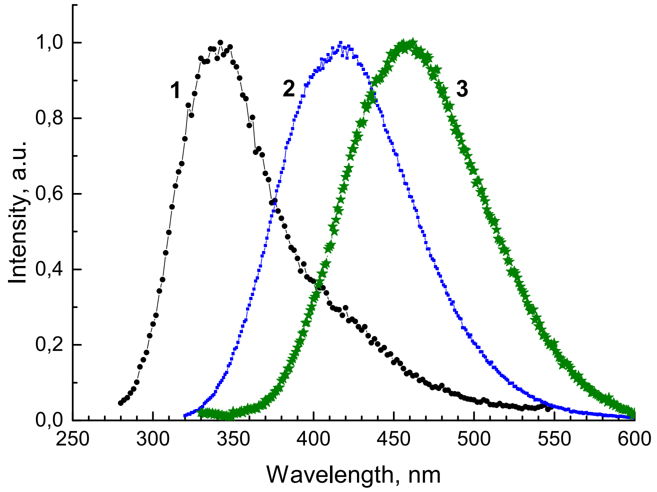


Fig. 1. Luminescence spectra of $\mathrm{YTaO_4}$ (λ_{ex} = 210 nm, 1) and $\mathrm{YNb_{0.6}Ta_{0.4}O_4}$ (λ_{ex} = 250 nm, 2 and λ_{ex} = 310 nm, 3), T = 300 K.

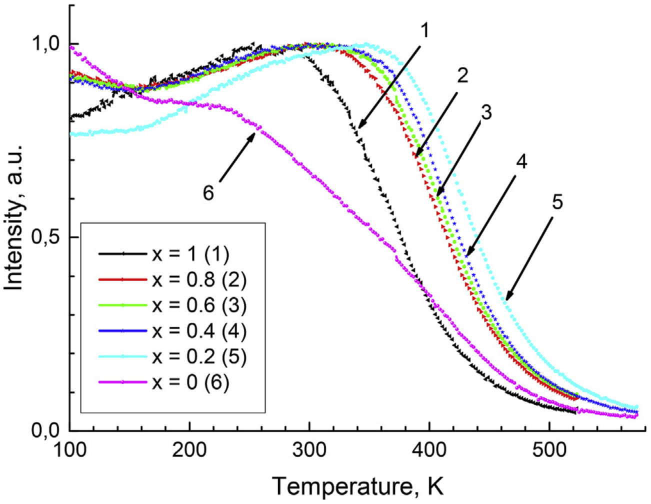


Fig. 2. The temperature dependence of luminescence intensity of $\mathrm{Y(Nb_xTa_{1-x})O_4}$ under X – ray excitation.

The onset of the excitation spectra of intrinsic luminescence shifts to higher energies with decrease of **x** (Fig. 3a). The shift is gradual but it is non-linear and the excitation spectra for heavily Nb-doped (**x** = 0.6, 0.8, 1) samples coincide. The effect is connected with the energy gap fluctuation which results in the appearance of the low-energy tails of DOS even at low Nb concentrations, i.e. with the local structure of mixed crystal [15]. However, the effect is less pronounced for the position of the defect related excitation band at 4.0–4.2 eV, whose shift can be traced even at high Nb concentrations (Fig. 3b). The excitation band is attributed to the electron transitions to defect level located in the bandgap. We suppose that the position of the defect energy level is determined by the averaged energy of the bottom of conduction band while the fluctuations of the bandgap results in the broadening of the excitation peak.

Several peaks are observed in the TSL curves in the region 100–320 K. (Fig. 4). No TSL peaks have been registered at T = 320–450 K, while their presence is reported in Ref. [25]. The TSL curve of $\mathrm{YNbO_4}$ was fitted by the sum of three elementary peaks in the approximation of first order kinetics with the following parameters of activation energies (E_i^{act}) and frequency factors (ω_i): E_1^{act} = 0.56 eV, ω_1 = $1.8*10^{12}$ s^{-1}, E_2^{act} = 0.49 eV, ω_2 = $3*10^{8}$ s^{-1}, and E_3^{act} = 0.62 eV, ω_1 = $1.2*10^{9}$ s^{-1}. The TSL curve of $\mathrm{YTaO_4}$ was fitted by the sum of four elementary peaks with E_1^{act} = 0.19 eV, ω_1 = $2*10^{4}$ s^{-1}, E_2^{act} = 0.2 eV, ω_2 = $2.3*10^{3}$ s^{-1}, E_3^{act} = 0.36 eV, ω_1 = $2.4*10^{6}$ s^{-1} and E_4^{act} = 0.55 eV, ω_4 = $3.2*10^{8}$ s^{-1}. The formula used for the approximation can be found elsewhere, e.g. Refs. [26,27]. The formation of TSL peak in the mixed crystals is more complicated than in its constituents. The mixed crystals are characterized by the presence of spatial fluctuations in the distribution of substitutional ions. It results in the appearance of the set of clusters with different dimensions in nanometer scale which are characterized by different bandgap values and shift of local trap levels [15]. As it follows from Fig. 4 the TSL peaks broaden for the mixed crystals because the peaks are combined by a set of clusters. The broadening has been also reported for the mixed