

SPECTROSCOPY OF Bi^{3+} -DOPED LANTHANIDE NIOBATES

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Introduction

The interest in Bi^{3+} -doped compounds has recently re-appeared in connection with the preparation of phosphors for new generation solid state light sources, so called WLED, where Bi^{3+} ions are used to efficiently absorb light in the near UV spectral range and transfer the energy to other emission centers in the green-red spectral range.

This work is devoted to the study of Bi^{3+} -doped lanthanide niobates. In previous studies, the emission and excitation spectra of Bi^{3+} -doped niobates were measured only at room temperature. Only investigations of the luminescence spectra and decay kinetics in a wide temperature range, including low temperatures, as well as the measurements of the luminescence intensity dependences on the Bi^{3+} concentration can allow to determine the origin and structure of the corresponding excited states.

The Bi^{3+} -related emission bands of two types having strongly different characteristics were revealed in Bi^{3+} -doped compounds (see, e.g., review papers [1-6] and references therein).

The ultraviolet emission, usually ascribed to the electronic transitions from the triplet excited state of a Bi^{3+} ion, has a relatively small Stokes shift and FWHM and the ms-decay time at 4.2 K, which remains constant up to 40-110 K indicating a large energy distance D between the emitting and metastable levels of the triplet excited state of Bi^{3+} . The visible emission is characterized by the large Stokes shift and FWHM and the temperature dependence of the decay time indicating a very small D value. Despite a huge number of publications, the origin of the VIS emission is still under discussion. This emission was ascribed to the metal-to-metal charge transfer, single Bi^{3+} ions, Bi^{3+} dimers, trapped or localized excitons, etc. Therefore, the detailed spectroscopic study and comparison of various Bi^{3+} -doped compounds is necessary in order to understand the reasons of different origin of the Bi^{3+} -related luminescence centers in different materials.

The aim of this work was to clarify the origin of the luminescence centers and their absorption (excitation) and emission bands, to determine the structure and parameters of the RES responsible for the intrinsic and Bi^{3+} -related luminescence and to investigate the processes taking place in the corresponding excited states.

The $\text{YNbO}_6:\text{Bi}$, $\text{LuNbO}_6:\text{Bi}$, and $\text{GdNbO}_6:\text{Bi}$ microcrystalline powders with different bismuth contents were synthesized by the standard solid-state reaction method. For all the investigated powders, the analysis of XRD patterns revealed pure monoclinic fergusonite-type structure. No traces of parasitic phases were detected.

Conclusions

The investigation of the photoluminescence characteristics of the undoped and Bi^{3+} -doped lanthanide niobates by the steady-state and time-resolved spectroscopy methods in a wide temperature range of 4.2-500 K and the determination of the structure and parameters of the corresponding triplet relaxed excited states (e.g., the probabilities of the radiative and non-radiative transitions from the emitting and metastable minima and the energy distance D between them) allows to make the justified conclusions on the origin of the observed emission bands. Only broad visible emission bands with the large Stokes shifts are observed in these compounds. These bands are found to arise from the triplet relaxed excited states characterized by a very low ($D < 1$ meV) spin-orbit splitting energy. This indicates the exciton-like origin of all the observed emission bands.

In Bi^{3+} -doped niobates, no ultraviolet emission caused by the radiative decay of the triplet relaxed excited state of a Bi^{3+} ion is observed. These data allow to conclude that the Bi^{3+} -related triplet relaxed excited state is located inside the conduction band. The dependences of the emission intensity on the Bi^{3+} content indicate that the complex visible emission band of the Bi^{3+} -doped niobates consists of two components arising from the excitons localized around the single Bi^{3+} ions and the $(\text{Bi}^{3+} - \text{Bi}^{3+})$ dimers (see also [7,8]).

It is concluded that under excitation in a Bi^{3+} -related absorption band, the ionization of Bi^{3+} takes place due to the location of the corresponding excited level inside the CB, and an electron is released into the CB. The subsequent immediate recombination of the optically released electron with the hole remained at the Bi^{3+} ion results in the formation of an exciton localized around the Bi^{3+} -related center. The radiative decay of this exciton results in the appearance of the exciton-like emission.

References

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Experimental results

The following properties were investigated: Photoluminescence characteristics under the steady-state excitation, luminescence decay kinetics and time-resolved emission and excitation spectra, temperature dependences of the luminescence intensity and decay time, concentration dependence of the luminescence intensity in undoped and Bi^{3+} -doped YNbO_6 , LuNbO_6 , GdNbO_6 powders with different Bi^{3+} contents. The obtained results are presented in Figs. 1-6.

Maxima positions of the emission (E_{em}) and excitation (E_{exc}) bands, full widths at half maximum (FWHM), and the Stokes shifts (S) of the emission bands obtained at 4.2 K for the investigated Bi^{3+} -doped lanthanide niobates as well as temperature (T_D) where the emission intensity decreases twice, the activation energy of luminescence thermal quenching (E_q), luminescence decay time (τ) at 4.2 K, and energy distance (D) between the emitting and metastable minima of the triplet localized exciton state are presented in Table.

Sample	E_{exc} , eV	E_{em} , eV	FWHM, eV	S , eV	T_D , K	E_q , eV	τ , μ s	D , meV
$\text{YNbO}_6:\text{Bi}$ [7]	STE	4.96	2.89	0.62	2.07	260	0.25	180
	$ex^0 \text{Bi}^{3+}$	4.09	2.53	0.53	1.56	250	0.22	33
	$ex^0 (\text{Bi}^{3+}-\text{Bi}^{3+})$	4.06	2.41	0.55	1.65	—	—	46
$\text{LuNbO}_6:\text{Bi}$	STE	5.04	2.91	0.64	2.13	205	0.12	149
	$ex^0 \text{Bi}^{3+}$	4.06	2.41	0.55	1.65	200	0.09	34
	$ex^0 (\text{Bi}^{3+}-\text{Bi}^{3+})$	3.97	2.32	0.55	1.70	—	—	40
$\text{GdNbO}_6:\text{Bi}$	STE	4.89	2.65	0.58	2.24	290	0.28	4.8
	$ex^0 \text{Bi}^{3+}$	4.11	2.64	0.57	1.47	310	0.21	4.4
	$ex^0 (\text{Bi}^{3+}-\text{Bi}^{3+})$	4.05	2.56	0.60	1.49	—	—	4.6

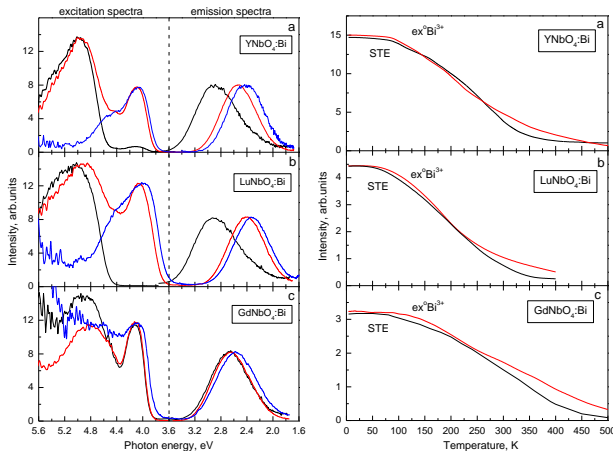


Figure 1. Steady-state emission and excitation spectra of (a) $\text{YNbO}_6:\text{Bi}$, (b) $\text{LuNbO}_6:\text{Bi}$ and (c) $\text{GdNbO}_6:\text{Bi}$ powders measured at 4.2 K for intrinsic emission (STE, black line), Bi^{3+} -related ($ex^0 \text{Bi}^{3+}$, red line) and ($ex^0 (\text{Bi}^{3+}-\text{Bi}^{3+})$, blue line) emissions. The spectra were measured in the best conditions for each emission and excitation bands.

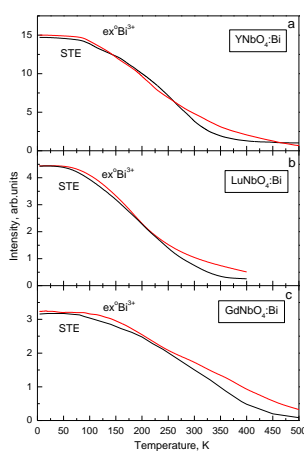


Figure 2. Temperature dependences of emission intensity in (a) $\text{YNbO}_6:\text{Bi}$, (b) $\text{LuNbO}_6:\text{Bi}$ and (c) $\text{GdNbO}_6:\text{Bi}$ powders measured at 4.2 K for intrinsic emission (STE, black line) and Bi^{3+} -related ($ex^0 \text{Bi}^{3+}$, red line) and ($ex^0 (\text{Bi}^{3+}-\text{Bi}^{3+})$, blue line) emissions. The spectra were measured in the best conditions for each emission band.

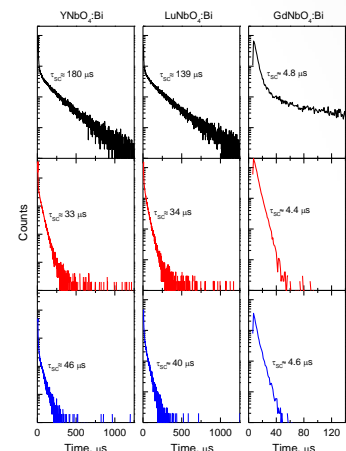


Figure 3. Luminescence decay curves measured at 4.2 K for intrinsic emission (STE, black line) and Bi^{3+} -related ($ex^0 \text{Bi}^{3+}$, red line; $ex^0 (\text{Bi}^{3+}-\text{Bi}^{3+})$, blue line) emissions of $\text{YNbO}_6:\text{Bi}$, $\text{LuNbO}_6:\text{Bi}$, $\text{GdNbO}_6:\text{Bi}$ powders under excitation with the xenon flash lamp. The decay curves were measured in the best conditions for each emission band.

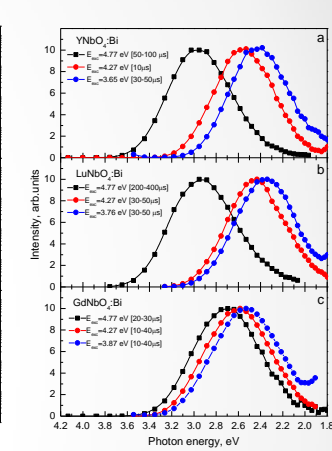


Figure 4. Time-resolved emission spectra measured at 79 K for (a) $\text{YNbO}_6:\text{Bi}$ and at 4.2 K for (b) $\text{LuNbO}_6:\text{Bi}$ and (c) $\text{GdNbO}_6:\text{Bi}$ powders under excitation in exciton (black squares) and in different ranges of Bi^{3+} -related absorption band (red and blue circles). The excitation energies (E_{exc}) used at the spectra measurements and the chosen time moments are shown in the legends.

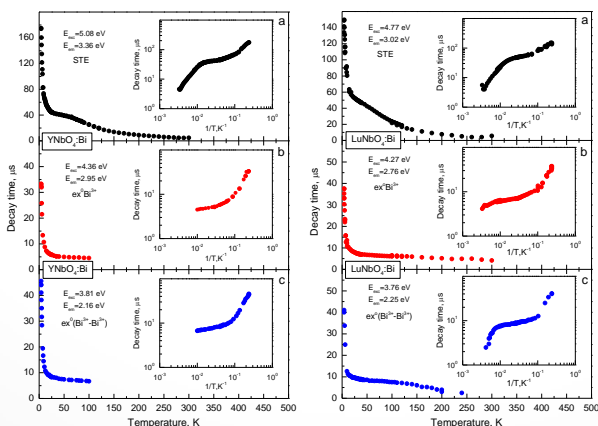


Figure 5. Temperature dependences of slow component decay time in $\text{YNbO}_6:\text{Bi}$, $\text{LuNbO}_6:\text{Bi}$, $\text{GdNbO}_6:\text{Bi}$ powders measured for (a) intrinsic emission (STE, black circles) and (b) Bi^{3+} -related ($ex^0 \text{Bi}^{3+}$, red circles; $ex^0 (\text{Bi}^{3+}-\text{Bi}^{3+})$, blue circles) emissions. In the insets, the corresponding decay time dependences on the reciprocal temperature. The emission (E_{em}) and excitation (E_{exc}) energies used at the measurements are shown in the legends.

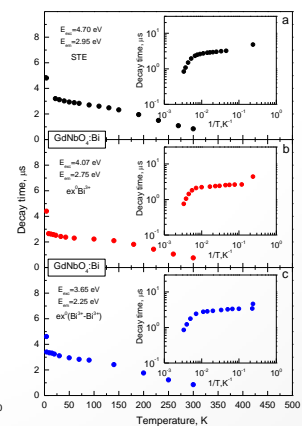


Figure 6. Dependences of the maximum luminescence intensity on the Bi content inside the niobates measured for the Bi^{3+} -related emission for (a) $\text{YNbO}_6:\text{Bi}$, (b) $\text{LuNbO}_6:\text{Bi}$ and (c) $\text{GdNbO}_6:\text{Bi}$ powders by the method described in [6-8].

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