SUMMARY

of the PhD Thesis on the specialty 6D072300 – Technical Physics
Assemgul Kissabekova "Spectroscopy of Bi^{3+}-doped lanthanide niobates as prospective materials for light-emitting diodes"

The purpose of research and scientific results.

The aim of this work is a detailed experimental study of the luminescence characteristics of several lanthanide niobates activated with Bi^{3+} ions ($YNbO_4$:Bi, $GdNbO_4$:Bi, $LuNbO_4$:Bi and $LuNbO_4$:Bi,Eu), as well as non-activated niobate $LuNbO_4$; elucidation of the nature of their emission bands; determination of the structure and parameters of the corresponding excited states of luminescence centers; elucidation of the mechanisms of the processes occurring in the excited states of luminescence centers. The aim of the study of niobate $LuNbO_4$:Bi, Eu is also to study the processes of energy transfer from Bi^{3+} ions to Eu^{3+} ions, which is necessary to assess possible practical applications of this material in white LEDs.

Research objectives. In dissertation work, the following particular scientific tasks were set and solved:

1. Investigation of the emission and excitation spectra, as well as the kinetics of luminescence decay in a wide temperature range (4.2 - 500 K) for Bi^{3+} -doped niobates $YNbO_4$, $GdNbO_4$, $LuNbO_4$, as well as for non-activated niobate $LuNbO_4$ and for mixed-doped (by Bi and Eu) $LuNbO_4$.
2. Luminescence intensity study of these materials depending on the Bi^{3+} concentration.
3. Find out the nature of the luminescence centers, as well as the absorption (excitation) and emission bands in these materials.
4. Determine the structure and parameters of excited states responsible for the intrinsic luminescence of these materials and for the luminescence associated with Bi^{3+} ions.
5. Investigate the mechanism of $Bi^{3+}\rightarrow Eu^{3+}$energy transfer in $LuNbO_4$:Bi,Eu samples and evaluate the possibilities of using this material in white LEDs.
6. Compare the photoluminescence and cathodoluminescence spectra in a wide temperature range for the niobates $YNbO_4$, $GdNbO_4$, $LuNbO_4$ activated by Bi^{3+} ions.

Research methods

In this work we have carried out a detailed and systematic investigation of Bi^{3+} -doped $LuNbO_4$ and $GdNbO_4$ powders with different Bi^{3+} content by the methods of the steady-state and time-resolved luminescence spectroscopy in the 4.2-500 K temperature range.

The cathodoluminescence characteristics of $YNbO_4$, $LuNbO_4$, $GdNbO_4$ doped with Bi^{3+} ions were measured under pulsed electronic excitation of ~ 100 keV with an electron beam penetration depth of more than 20 μm.

Statements for the defense:

1. The broad emission bands of non-activated and activated Bi^{3+} lanthanide niobates $YNbO_4$, $GdNbO_4$, $LuNbO_4$ with large Stokes shifts are due to transitions from the triplet excited state of the luminescence center. The relatively low (~1 meV) spin-orbit splitting energy of this state indicates the exciton-like nature of all the observed emission bands; the triplet relaxed excited state of the Bi^{3+} ion is located inside the conduction band. In the materials under study, there is no radiation caused by the radiative decay of the triplet relaxed excited state of the Bi^{3+} ion (i.e., electronic transitions $^3P_1\rightarrow {}^1S_0$). Luminescence of

an excitonic nature arises as a result of photostimulated electronic transitions from the ground state of the Bi^{3+} ion to its triplet excited state, corresponding to ${}^1S_0 \rightarrow {}^3P_1$ transitions of the free Bi^{3+} ion.

2. The dependences of the radiation intensity of niobates activated by Bi^{3+} ions on the bismuth concentration in the samples under study show that the complex visible emission band of these materials consists two components arising from the radiative decay of excitons localized near single Bi^{3+} ions and near {Bi^{3+} -Bi^{3+}} dimers.

3. The energy transfer from the luminescence centers associated with Bi^{3+} ions to Eu^{3+} ions in LuNbO4: Bi, Eu niobate was discovered, and the opportunity of using this material in white light-emitting diodes was evaluated.

4. Intense broad cathodoluminescence bands of YNbO4: Bi, GdNbO4: Bi, LuNbO4: Bi niobates have a complex structure and are a superposition of several bands of an excitonic nature. Weak ultrafast radiation in the ultraviolet region of the spectrum belongs to the so-called intraband luminescence.

Scientific results

The study of nonactivated and activated Bi^{3+} lanthanide niobates in a wide temperature range (4.2 - 500 K) under both stationary and pulsed photoluminescence excitation were made, it was found that the broad emission bands of these materials with large Stokes shifts are due to transitions from the triplet excited state of the luminescence center. The relatively low (~ 1 meV) spin-orbit splitting energy of this state indicates the exciton-like nature of all the observed emission bands. From obtained data the triplet relaxed excited state of the Bi^{3+} ion is located inside the conduction band. This conclusion explains the absence of radiation in the materials under study caused by the radiative decay of the triplet relaxed excited state of the Bi^{3+} ion (i.e., electronic transitions ${}^3P_1 \rightarrow {}^1S_0$). The appearance of luminescence of an excitonic nature occurs as a result of photostimulated electronic transitions from the ground state of the Bi^{3+} ion to its triplet excited state, corresponding to ${}^1S_0 \rightarrow {}^3P_1$ transitions of the free Bi^{3+} ion.

From the dependence of the radiation intensity of niobates activated by Bi^{3+} ions on the dopant concentration in the considered samples, it was concluded that the complex visible emission band consists of two components arising from the radiative decay of excitons localized near single Bi^{3+} ions or near {Bi^{3+}-Bi^{3+}} dimers.

It was found that in niobates $LuNbO_4$:Bi,Eu there is an effective nonradiative energy transfer from excited Bi^{3+} ions to Eu^{3+} ions.

Comparative analysis of cathodoluminescence and photoluminescence allows us to conclude that intense broad cathodoluminescence bands of all studied niobates also have a complex structure, they present a emission bands superposition of self-trapped (matrix) excitons and excitons localized near single impurity Bi^{3+} or their dimers {Bi^{3+} -Bi^{3+}}. The presence of weak ultrafast radiation in the ultraviolet region of the spectrum, which is the so-called intraband luminescence, is shown.

Scientific novelty and practical significance of the research outcomes. The scientific novelty and theoretical significance of the research results are as follows:

For the first time, a detailed study of the photoluminescence characteristics of Bi^{3+} -activated lanthanide niobates $YNbO_4$, $LuNbO_4$, and $GdNbO_4$ and unactivated niobate $LuNbO_4$ was carried out in a wide temperature range (4.2 - 500 K) both under stationary excitation and by time-resolved spectroscopy, which made it possible to establish the exciton nature of these materials.

The measurements of the dependences of the luminescence intensity on the Bi^{3+} concentration, which made it possible to determine that the complex visible radiation band of Bi^{3+} doped niobates consists two components caused by excitons localized near single Bi^{3+} ions and near the $\{Bi^{3+}$ -$Bi^{3+}\}$ paired centers.

The processes leading to the appearance of radiation of an excitonic nature upon excitation of the investigated materials in the absorption band of Bi^{3+} ions are considered.

The details of energy transfer mechanism from Bi^{3+} ions to Eu^{3+} ions in $LuNbO_4$:Bi, Eu samples and the efficiency dependence of such energy transfer due Eu^{3+} concentration have been studied in detail.

The luminescence quantum yields for the $LuNbO_4$: Bi,Eu and the CIE chromaticity coordinates have been determined, and the opportunity of using this material in white LEDs has been evaluated.

A comparison is made of the photo- and cathodoluminescence spectra in a wide temperature range for the niobates $YNbO_4$, $GdNbO_4$, $LuNbO_4$ activated with Bi^{3+} ions.

The obtained results show that the most promising from view of practical applications can be materials doped with Bi^{3+} ions possessing broad emission bands of an exciton nature in the visible region of the spectrum, i.e. materials in which the lowest excited state of the Bi^{3+} ion is located above the bottom of conduction band. The results obtained can be used as a basis for further optimization of bismuth-doped lanthanide niobates in order to obtain inexpensive and efficient phosphors for white LEDs, as well as field emission displays.

Compliance with directions of development of science or government programs

The dissertation work corresponds to the priority directions of the development of science, which are being implemented in the Republic of Kazakhstan and contains new scientifically substantiated results, the totality of which is important for the development of the research areas under study.

Personal contribution of the PhD student.

The results presented in the dissertation were obtained personally by the author, as well as jointly with the staff of the Laboratory of Physics of Ionic Crystals of the Institute of Physics of the University of Tartu (Tartu, Estonia) and at the Institute of Physics of the Polish Academy of Sciences, which is reflected in the publications.

Discussion and analysis of the results were carried out jointly with supervisors, as well as with Doctor of Phys.-Math. Sciences Zazubovich S.G., and PhD in Physics Krasnikov A.S.

The obtained results were published in 8 publications, including 6 thesis’s in proceedings of international scientific conferences, and 2 articles in journals indexed Web of Science (Thomson Reuters) and Scopus information resources.

The results of the work were discussed at international conferences: 20th International Conference on «Radiation Effects in Insulators» (Nur-Sultan, Kazakhstan 2019); 7th International Congress on «Energy Fluxes and Radiation Effects» (Tomsk, Russia, 2020); 9th international conference on «Radiation in various fields of research» (Herzeg-Novi, Montenegro, 2021); 8 International Conference on «Физика. Технологии. Инновации» (Yekaterinburg, Russia, 2021), International Conference on «Тенденции развития физики конденсированных сред» (Fergana, Uzbekistan, 2021).