LUMINESCENCE OF Pr^{3+} IONS AND RADIATION-INDUCED DEFECTS IN COMPLEX INORGANIC COMPOUNDS

S.A. Kiselev[1], *V.A. Pustovarov*[1],
K.V. Ivanovskikh[1,2], *Q. Shi*[3],
M.O. Kalinkin[4], *M.O. Petrova*[5]

[1] Ural Federal University, Ekaterinburg, Russia
[2] GIREDMET State Research & Design Institute of Rare Metal Industry, Moscow, Russia
[3] College of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan, China
[4] Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia
[5] Joint Institute for Nuclear Research, Dubna, Russia

e-mail: sviat-kiselev@yandex.ru

ЛЮМИНЕСЦЕНЦИЯ ИОНОВ Pr^{3+} И РАДИАЦИОННО-ИНДУЦИРОВАННЫХ ДЕФЕКТОВ В КОМПЛЕКСНЫХ НЕОРГАНИЧЕСКИХ СОЕДИНЕНИЯХ

С.А. Киселев[1], *В.А. Пустоваров*[1],
К.В. Ивановских[1,2], *Ц. Ши*[3],
М.О. Калинкин[4], *М.О. Петрова*[5]

[1] ФГАОУ ВО «УрФУ им. первого Президента России Б.Н. Ельцина», Екатеринбург, Россия
[2] АО «Гиредмет» им. Н.П. Сажина, Москва, Россия
[3] Колледж Физики и Оптоэлектроники, Тайюаньский Технологический Университет, Тайюань, Китай
[4] ФГБУН Институт химии твердого тела УрО РАН, Екатеринбург, Россия
[5] Объединенный институт ядерных исследований, Дубна, Россия

Abstract

Spectroscopic properties of complex oxide materials, i.e. silicates, germanates and phosphates, doped with Pr^{3+} impurity ions are presented in this report. Defect related phenomena have been understood via studying of non-irradiated samples in comparison with those irradiated with fast electrons (E = 10 MeV) and fast neutrons. The main channels for radiative relaxation include interconfigurational 5d → 4f transitions, intraconfigurational 4f → 4f transitions and defect-related luminescence. The presence and structure of the defects have been confirmed and studied with EPR.

Keywords: *phosphates, luminescence, rare earth ions, praseodymium, 5d → 4f transitions, 4f → 4f transitions, energy transfer, radiation-induced defects*

Аннотация

В работе исследованы спектроскопические свойства комплексных оксидных соединений – силикатов, германатов, фосфатов, легированных ионами Pr^{3+}. Исследования проводились на необлученных образцах и после их облучения быстрыми электронами (E = 10 МэВ) и быстрыми реакторными нейтронами. Выявлены три типичных канала излучательной релаксации электронных возбуждений: межконфигурационные 5d → 4f переходы, внутриконфигурационные 4f → 4f переходы в ионах Pr^{3+} и люминесценция, связанная с дефектами. После облучения активно проявляются новые центры эмиссии, наличие и структура которых подтверждается ЭПР-исследованиями.

Ключевые слова: *люминесценция, редкоземельные ионы, празеодим, 5d → 4f переходы, 4f → 4f переходы, перенос энергии, радиационно-индуцированные дефекты*

Microcrystalline powders of $Sr_3Lu_2Ge_3O_{12}$, $Ba_9Lu_2Si_6O_{24}$, $KLuP_2O_7$, $Sr_9Sc(PO_4)_7$, $K_3Lu(PO_4)_2$, doped with impurity Pr^{3+} ions were synthesized via solid state reaction and PXRD verified at Taiyuan University of Technology. Spectroscopic studies were performed using various techniques, including measurements of photoluminescence spectra (PL) upon selective UV-excitation, PL excitation spectra, decay kinetics upon pulsed cathode excitation, and electron paramagnetic resonance (EPR) spectra in the temperature range of T = 110 – 300 K. The above-mentioned materials when doped with rare-earth (RE) ions are considered to be promising for various scintillator applications, such as medical imaging, dosimetry, radiation monitoring, nuclear physics, etc. Most properties of RE-ions depend on inter- or intraconfigurational transitions within 4*f* or between 4*f* and 5*d* states, respectively. As demonstrated in [1, 2] Pr^{3+} ions provide faster decay of interconfigurational *5d* → *4f* transitions in comparison to that observed for widely applied Ce^{3+} ions (15-30 ns vs. of 30-60 ns in Ce^{3+}), while Pr^{3+} emission is characterized by higher energy. Interconfigurational transitions can be observed in Pr^{3+} when strong enough crystal field shifts the lower excited $4f^{1}5d^{1}$ state below $^1S_0$ state of the main $4f^2$ electron configuration. The *5d* →

4f transitions dominate in luminescence spectra subject to several conditions, the most crucial of which is the need of sufficient Stokes shift (~ 0,4 eV or greater). While performing multiple luminescence spectroscopic studies of the materials involved in the present study we found that the most significant quantum yield is observed for the phosphates. Thus they were chosen for further investigation of their radiation stability upon electron or neutron radiation. The electron beam irradiation was performed using 10 MeV linear electron accelerator at Ural Federal University. The fast neutron irradiation was performed at the IBR-2 reactor at Joint Institute for Nuclear Research. The PL and PCL spectra within the temperature range of 5-300 K were recorded at Ural Federal University. The EPR spectra were studied at Institute of Solid State Chemistry (UB RAS). As expected, all the samples demonstrated a typical luminescence properties of Pr^{3+} ions. Fig. 1 shows representtative results of PL spectra measurements for $KLuP_2O_7:Pr^{3+}$ (1 %). The results suggest that before the irradiation the main channel for radiative decay is through interconfigurational transitions observed within the 250-320 nm region. PCL decay kinetics recorded at Pr^{3+} emission band reveal an average decay time of 20 ns. Narrow line features of intraconfigurational *4f* → *4f* transitions are weekly observed around 600 -610 nm. A defect-related luminescence observed in the range of 400-600 nm drastically increases in intensity after electron irradiation. As demonstrated by the means of PL excitation measurements, there is an efficient energy transfer from impurity Pr^{3+} ions to the lattice defects as both of them are most efficiently excited at 5.5 eV. These observations suggest that the defects act as competitive channel for capture of charge carriers. Both electron- and neutron-irradiated samples showed similar behavior of defect-related luminescence, and its intensity increases proportionally to the dose applied.

By comparing the recorded spectra with previously published data [3-8], the nature and structure of the observed defects was proposed. The crystal structure of the studied phosphates contains tetrahedral complexes [PO_4], therefore, defects similar to those in SiO_2 glasses should be expected [5, 6]. Such defects are formed when the P=O bond breaks with the formation of a $(PO_4)^{2-}$ radical (defects of P1 type according to the classification [3, 4]) that represents a non-bridged oxygen atom or the formation of oxygen-deficient center. Note that $(PO_4)^{2-}$ radicals are characteristic point defects for a number of complex phosphate compounds [3, 4, 7, 8]. However, similar to SiO_2, the $(PO_4)^{2-}$ radical cannot stabilize in a regular crystal structure [5, 6]. The formation of stable defects presupposes its local amorphization after an irradiation. On the other hand, a comparative analysis PL spectra recorded in this work with the spectroscopic data published on defects of type P4 [3] corresponding to the radical $(PO_2)^{2-}$. The latter suggest bonding between a phosphorus atom and two oxygen atoms in a tetrahedral structure [PO_4]. This type of defects is known to well manifest in ESR spectra [4]. Our ESR measurements performed for the studied samples confirmed the aforementioned assumption. Both PL and ESR measurements demonstrated more efficient capture of charge carriers at low temperatures.

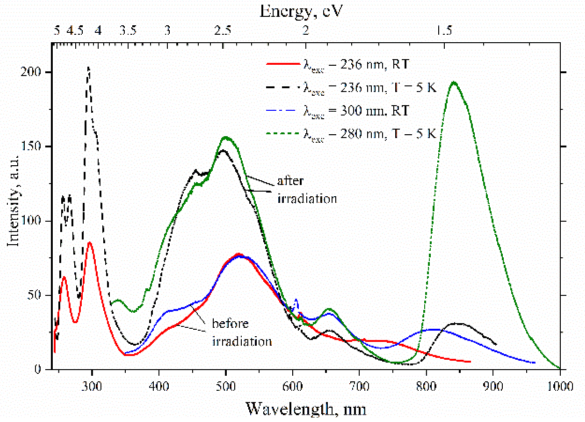

Fig. 1. PL spectra of $KLuP_2O_7:Pr^{3+}$ (1 %) upon UV-excitation (λ_{exc}), at T = 5 and 300 K before and after neutron irradiation

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