Luminescence of praseodymium doped perovskite — like $SrLa_4Ti_5O_{17}$ under excitation with VUV and UV synchrotron radiation

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The wide-band complex spectra of intrinsic luminescence of undoped $SrLa_4Ti_5O_{17}$ compounds are found in range of 350–1100 nm under excitation by the light from ultraviolet and vacuum ultraviolet range (50–334 nm) of synhrotron radiation. The possible origines of the observed luminescence are associated with peculiarities of the structure of the layered perovskite-like $SrLa_4Ti_5O_{17}$ compound. So, three luminescence components of the intrinsic luminescence peaked near ~ 530, ~ 830, and ~ 1100 nm have been attributed to the radiation decay of excitons localized on $(TiO_6)^{8-}$ molecular groups of three types in the lattice of $SrLa_4Ti_5O_{17}$. The luminescent features related with $4f \rightarrow 4f$ and $4f5d \rightarrow 4f$ radiation transitions in Pr^{3+} ions are found in addition to mentioned intrinsic emission for the $SrLa_4Ti_5O_{17}$ compound doped with Pr^{3+} ions. Obtained results show the prospects of the $SrLa_4Ti_5O_{17}$ compounds doped with Pr^{3+} ions to be used as luminophores of wide emission spectra.

Keywords: perovskite, titanate, praseodymium ion, intrinsic, luminescence.

Сложные, широкополосные спектры собственной люминесценции нелегированных соединений $SrLa_4Ti_5O_{17}$ выявлены в диапазоне 350–1100 нм при возбуждении светом из диапазона ультрафиолетового и вакуумно-ультрафиолетового синхротронного излучения (50–334 нм). Наблюдаемая люминесценция связывается с особенностями структуры слоистых перовскитоподобных соединений $SrLa_4Ti_5O_{17}$. Компоненты собственной люминесценции с максимумами при ~ 530, ~ 830 и ~ 1100 нм приписаны излучательному распаду экситонов, локализованных на молекулярных группах трех типов в решетке $SrLa_4Ti_5O_{17}$. Люминесценция, связанная с известными $4f \rightarrow 4f$ и $4f5d \rightarrow 4f$ излучательными переходами в ионах Pr^{3+}, обнаружена для соединения $SrLa_4Ti_5O_{17}$ легированного ионами Pr^{3+}. Полученные результаты показали перспективность использования соединений $SrLa_4Ti_5O_{17}$, легованных ионами Pr^{3+}, как люминофоров широкого спектра излучения.

Люмінесценція легованого празеодимом перовськітоподібного $SrLa_4Ti_5O_{17}$ при збудженні ВУФ та УФ синхротронним випромінюванням. *С.Неділько, В.Чумак, Ю.Тітов.*

Широкосмугові складні спектри власної люмінесценції нелегованих сполук $SrLa_4Ti_5O_{17}$ виявлено у діапазоні 350–1100 нм при збудженні світлом із діапазону ультрафіолетового і вакуумно-ультрафіолетового синхротронного випромінювання (50–334 нм). Спостережена люмінесценція пов'язується із особливостями структури шаруватих перовськітоподібних сполук $SrLa_4Ti_5O_{17}$. Компоненти власної люмінесценції із максимумами при ~ 530, ~ 830 та ~ 1100 нм приписано випромінювальному розпаду екситонів, локалізованих на молекулярних групах трьох типів в решітці $SrLa_4Ti_5O_{17}$. Люмінесценція із відомими $4f \rightarrow 4f$ та $4f5d \rightarrow 4f$ випромінювальними переходами в іонах Pr^{3+}, знайдено для сполуки $SrLa_4Ti_5O_{17}$ легованої іонами Pr^{3+}. Одержані результати показали перспективи використання легованих іонами Pr^{3+} сполук $SrLa_4Ti_5O_{17}$ як люмінофорів широкого спектра випромінювання.

1. Introduction

The materials those reveal visible luminescence under vacuum ultraviolet (VUV) or ultraviolet radiation (UV) are needed for plasma displays and mercury-free fluorescent lamps. Vacuum luminescenct displays and self-electron (field) emission displays are also devices of mentioned materials possible usage. Both undoped and doped with ions of the rear-earth elements (RE) the oxide materials are very important in high energy physics, medical diagnostic etc. as scintillators and detectors of ionizing radiation and particles with the high energetic and time resolution.

A lot of important properties, such as ferro- and piezoelectric, electretes, optical unliniarity etc. of the layered perovskite-like structure (LPS) compounds of $A_nB_nO_{3n+2}$ (A = Ca, Sr, Pb, La ÷ Sm; B = Ti, Nb, Ta, Fe, Sc) family (n = 2 ÷ 6 is a number of BO_6 octahedra) [1], have promoted to synthesis and determination of the structure of compounds and isomorphycally substituted phases of this family, particularly those that are based on the five-layered titanates $A^{II}Ln_4Ti_5O_{17}$ (A^{II} = Ca, Sr, Ln = La, Pr, Nd) [2–7].

Unfortunately, compounds of the $A_nB_nO_{3n+2}$ family were not studied before as optical materials. Although, one could expect a manifestation of a number of the optical properties, in particular luminescent, for them as the composition of their LPS is similar to the composition of the perovskite structure alkaline earth titanates $A^{II}TiO_3$ (A^{II} = Mg, Ca, Sr, Ba). The last ones manifest luminescent properties and they are very attractive due to spectral distribution and intensity of their emission, especially when they are doped with three plus RE ions (RE^{3+}) and additive co-dopping takes place [8–11]. Study of the alkaline earth titanates doped with praseodymium ions Pr^{3+} ($A^{II}TiO_3$:Pr^{3+}) have shown that these compounds could be applicated as effective photoluminofors in elaboration of minisized luminescent lamps and light emitting diodes (LEDs) [12, 13]. Luminescence of the Pr^{3+} ions doped oxides, make them as materials perspective not only for mentioned applications. They are also discussed as very promising scintillation materials, those are able to simultaneously provide high light yield and fast decay of the scintillation pulses. The behavior of the allowed <-->4f dipole transitions in Pr^{3+} ions causes the noted above characteristics [14–16]. As had been shown before, luminescence of the praseodymium ions in solids can be managed by changing the solids lattice composition, crystal grains sizes changing, etc [17]. So, the doped with Pr^{3+} ions solids are suitable objects for luminophors and scintillators engineering. The doped with Pr^{3+} ions $SrLa_4Ti_5O_{17}$ crystals were studied by us, and their composition and structure could allowed us a good opportunity for luminescent properties management.

Really, two dimensional (un-finited in X and Z axes directions) perovskite-like blocks, those composed from five slabs of deformed octahedra TiO_6 are the main elements of the $SrLa_4Ti_5O_{17}$ LPS lattice (Fig. 1) [2].

The degree of TiO_6 octahedra distorsion (Δ) in the $SrLa_4Ti_5O_{17}$ structure is minimal for the $Ti(3)O_6$ octahedron located in the center of the perovskite-like block (Δ = $19 \cdot 10^{-4}$ nm) and average distance between titan and oxygen atoms of this octhaedron, <Ti(3),O> is 0.196 nm. The $Ti(1)O_6$ and $Ti(2)O_6$ octahedra, which located on the border of the neighbouring block, differ by the deformation degree and especially if to compare with central $Ti(3)O_6$ octahedron deformation. In fact, Δ = $38 \cdot 10^{-4}$ and $45 \cdot 10^{-4}$ nm for the $Ti(1)O_6$ and $Ti(2)O_6$ octahedra, respectively [2].

The perovskite-like blocks are separated by the layers of distorced and jointed by the common edges $(Sr,La)O_9$ ninevertex, so there is no direct connection between TiO_6 octahedrons which are placed on the borders of the neighbouring perovskite-like blocks. The blocks are connected due to $-O-(Sr,La)(1)-O-$ interblock bonds. Located on the border between the blocks the (Sr,La)(1) atoms are surrounded by seven oxygen atoms (2O(4), O(6), 2O(7), 2O(8)) of the same blocks and by two (O(4) and O(7)) oxygen atoms of the neighbouring blocks on the distances ranging from 0.240 to 0.314 nm (the average distance is 0.267 nm). Coordination number of the intrablock atoms (Sr,La)(2) and (Sr,La)(3) in the $SrLa_4Ti_5O_{17}$ structure is 12, and their coordination polyhedrons are distorted cubooctahedrons (Fig. 1). The distances (Sr,La)(2)–O are in the range from 0.240 to 0.306 nm (the average distance is 0.280 nm), while for the (Sr,La)(3) atoms the (Sr,La)(3)–O distances are in the range from 0.241 to 0.311 nm (the average distance is 0.271 nm). If in the first case there are four oxygen atoms lying at the same distance from the (Sr,La)(2) atom, then for the (Sr,La)(3) position, the four oxygen
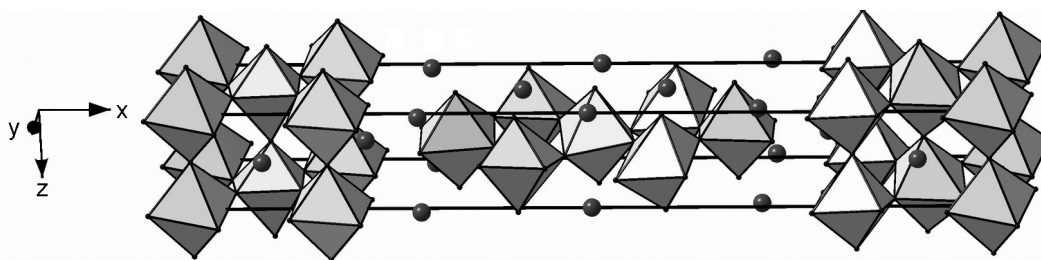
Fig. 1. Crystal structure of $SrLa_4Ti_5O_{17}$ LPS is shown as TiO_6 octaedrons, Sr and La (circles) [2].

atoms lie in pairs at identical distances, but they lie at the different distances for each pair. That is, deformation of the oxygen polyhedrons of (Sr,La) atoms in different positions, as well as the mean (Sr,La)−O distances are different.

Thus, according to our previously performed studies, we can state the similarity of the $SrTiO_3$ perovskites and layered $SrLa_4Ti_5O_{17}$ compounds lattice structure; presence of three types of TiO_6 octahedra with different degree of deformation in the structure of the $SrLa_4Ti_5O_{17}$ titanate and presence of three types of La/Sr atoms positions there. This multivariantness is the $SrLa_4Ti_5O_{17}$ crystal properties managment tool, we suppose.

So, the task of this work was to detect a possible manifestation of un-doped and doped with praseodymium ions $SrLa_4Ti_5O_{17}$ titanate luminescence, determine spectral and kinetic characteristics of the luminescence and to describe its possible mechanisms.

Bond to bond transition with absorption of light in the undoped compounds like to discussed here have to occurred under energy of exciting light quanta higher than ~ 3.5 eV. The Pr^{3+} ions can be also excited at similar energies due to $5d{\leftrightarrow}4f$ and $4f{\leftrightarrow}4f$ absorption transitions. Therefore, in this work, the luminescent properties of the $SrLa_4Ti_5O_{17}$ compound are studied in large range of exciting wave length from VUV and UV diapasons at temperature near 10 K. Cooling to this temperature makes it possible to simplify the analysis of spectral and kinetic data due to the "freezing" of vibronic processes and thermal over-barriers transfer of the excitation energy. This simplification at the initial stage of studying the mechanisms of luminescence in these systems is expedient, in our opinion.

2. Experimental

Synthesis of the samples was made by heat treatment ($T = 1670$ K, t — 2 h) of co-precipitated hydroxycarbonates batch. Aqueous solutions of $Sr(NO_3)_2$, $La(NO_3)_3$, $Pr(NO_3)_3$ and $TiCl_4$ (c.p. grade) were used as starting materials. Aqueous buffer solution of $NH_4OH + (NH_4)_2CO_3$ with pH $\approx$ 8.5 was used as a precipitating agent. In applying this procedure, the mixing of components occured at the ion-molecular level in aqueous solution and allows for absolutely uniform distribution of dopants in the sample volume. Details of the sample preparation are available also in [5, 6] and in other published papers of the authors of this work.

In order to minimize the destruction of the $SrLa_4Ti_5O_{17}$ crystalline lattice and prevent the processes of luminescence quenching due to the so-called, cross-relaxations which were actual at the high praseodymium concentrations, the amount of the praseodymium dopant was only 0.001 mol.%.

X-ray diffraction studies of the polycrystalline powder samples were carried out with use of DRON-3 diffractometer ($CuK\alpha$ radiation, Ni-filter). XRD patterns were taken using step by step regime. Step scan was 0.03°, counting time per step — 5 s.

Experiments with using synchrotron radiation were made at SUPERLUMI station of HASYLAB (DESY) synchrotron, Hamburg, Germany. The primary 2 m normal incident light monochromator in 15° Mc Pherson mounting had a working UV and VUV spectral range of 25−334 nm (50−3.7 eV) and a spectral resolution of 0.3 nm. The spectra of luminescence excitation of compounds under study were measured in the range of excitating wave length, λ_{ex}, 50−334 nm (25−3.7 eV). Luminescence spectra were measured in the range of 300−1100 nm using registering ARC 0.3 m Czerny-Turner monochromator/spectrograph "Spectra Pro 300i" (f/4) which had resolution interval $\Delta\lambda > 0.1$ nm and three interchangeable gratings. The detectors were a liquid nitrogen cooled CCD detector from Princeton Instruments (200−1100 nm) and HAMAMATSU R6358P photomultiplier (200−800 nm).
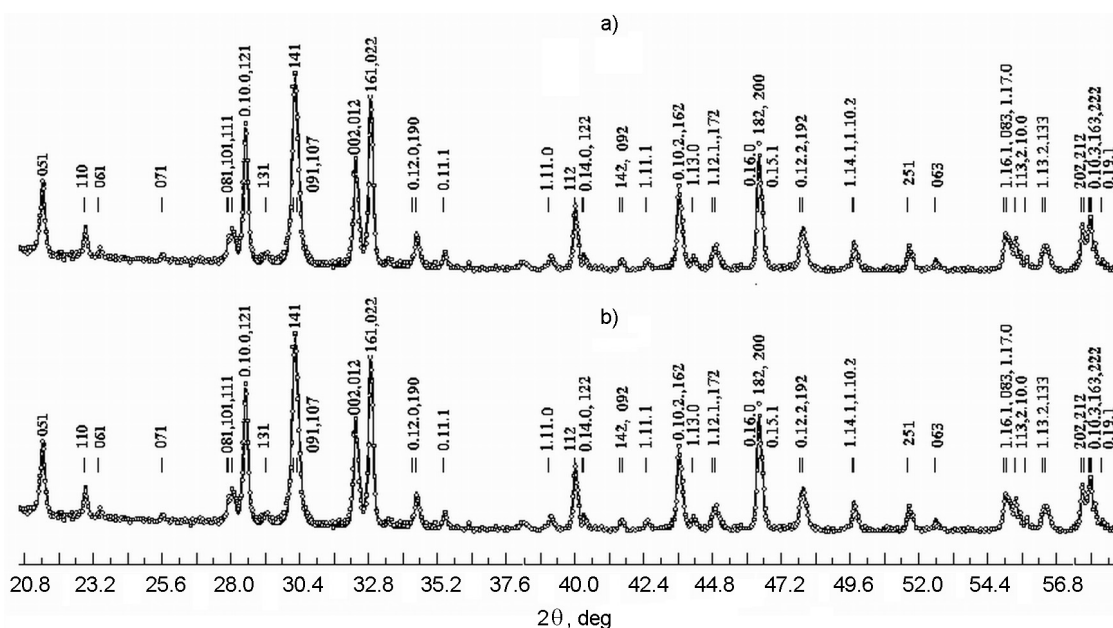
Fig. 2. XRD patterns of $SrLa_{4-x}PrTi_5O_{17}$ powders; $x = 0$ (a) and 0.001 (b).

3. Results and discussion

In order to evaluate a possible influence of praseodymium dopant on the structure and parameters of the $SrLa_4Ti_5O_{17}$ lattice a comparative analysis of the XRD patterns of undoped $SrLa_4Ti_5O_{17}$ and doped with praseodymium $SrLa_4Ti_5O_{17}:Pr^{3+}$ powders was made. As Fig. 2 shows, there are no influence of the dopant on the set, positions and intensity of the reflexes inherent to the undoped $SrLa_4Ti_5O_{17}$.

Luminescence of the undoped $SrLa_4Ti_5O_{17}$ compound under excitation in the range of synchrotron radiation from 50 to 334 nm (the last value is defined by the upper limit of the working range of the "SUPERLUMI" station) can be found in the wide range of wave lengths from 325 up to 1100 nm, that is, the one that covers soft UV, visible and near-infrared light (Fig. 3). The wide band of photoluminescence (PL) is obviously complex. So, at the shortest wave length excitation, $\lambda_{ex} = 78$ nm, two component, at least, can be highlighted in the PL band composition. This is shorter wave length component that lies in the range of visible light, 360–750 nm with peak position, λ_{max}, near 580 nm, and the longer wave length, IR component, that is manifested as shoulder on the background of the visible emission. It lies in the range of 700–1100 nm and has hidden maximum in the vicinity of 800–850 nm (Fig. 3, curve 1). The same components form the PL spectrum at the longer wave length VUV excitations. However,

relative contribution of the IR emission component rises at λ_{ex} rising. Thus, the IR component is separated and has a maximum near 830 nm at $\lambda_{ex} = 150$ nm. (Fig. 3, curve 2). The contribution of the IR component to the total PL spectrum continues to increase at further increasing wavelength of excitation. If the λ_{ex} reaches the values >300 nm, the long-wavelength side of the PL IR component extends beyond the operating range of the "SUPERLUMI" station registering monochromator (Fig. 3, curve 3).

When praseodymium ions were added to composition of the $SrLa_4Ti_5O_{17}$ compound (the $SrLa_4Ti_5O_{17}:Pr$ sample) the set of lines arouse in the PL spectra on background of the bands of the own luminescence of host matrix. The group of lines in vicinity of 585–645 nm shows maximal intensity, and line near 610 nm is the most intensive among them. The lines located at the shorter wave lengths in the ranges of 480–520 and 530–580 nm are of the lower intensity and they are strongly overlaped. Spectral details located at the longer wave length than mentioned main line (~ 680–740, 750–810, 810–860, and 870–930 nm) are also not very pronounced in relation to the main line and the broadband background. Intensity of the lines and those ratio to intensity of the background bands depend on the excitation wave length. The PL spectra of the $SrLa_4Ti_5O_{17}:Pr$ compound at $\lambda_{ex} = 78$, 150, and 307 nm are given on in Fig. 4 for example.

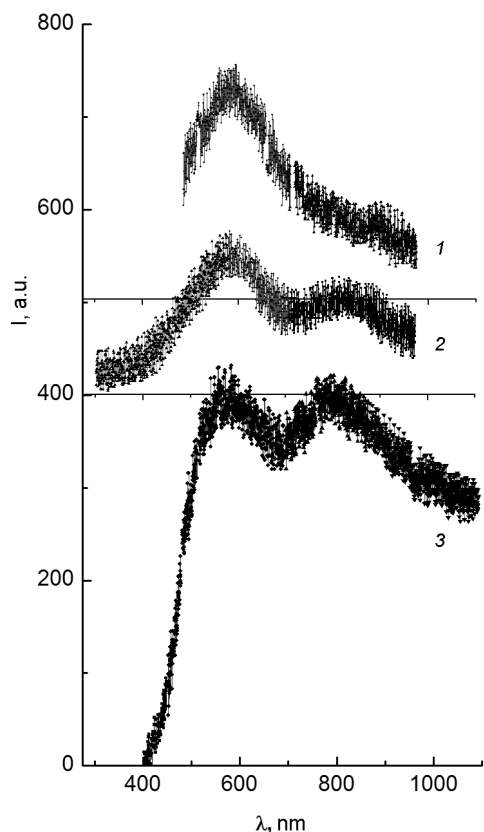Fig. 3. Luminescence spectra of un-doped SrLa$_4$Ti$_5$O$_{17}$ crystals; λ_{ex} = 78, 150, and 307 nm; T = 10 K.

It should be noted, that besides of described above lines, a wide band is observed in the range of 330–450 nm for doped crystal comparing to the PL spectra of the undoped crystal. (This band is marked by arrow in Fig. 4). Intensity of this band is lower than intensity of mentioned before wide luminescence bands both at short wave length, 78.3 nm, and longer, 150 nm, excitations (Fig. 4).

Spectra of luminescence excitation for the undoped, SrLa$_4$Ti$_5$O$_{17}$, and doped, SrLa$_4$Ti$_5$O$_{17}$:Pr, being registereding not far from maximum of intensive band, λ_{reg} = 530 nm, and near the line of maximal intensity, λ_{reg} = 610 nm, are shown in Fig. 5, curves 1 and 2, respectively. In these spectra, according to the characteristic features, it is possible to specify such regions as 50–125, 125–185, and 185–334 nm. At the same time, it is easy to see certain differences between the indicated spectra. So, in the excitation spectrum of the wide band PL of the undoped SrLa$_4$Ti$_5$O$_{17}$ the intensive structureless band is observed within the first of these regions. The band of lower intensity takes places also in the region of
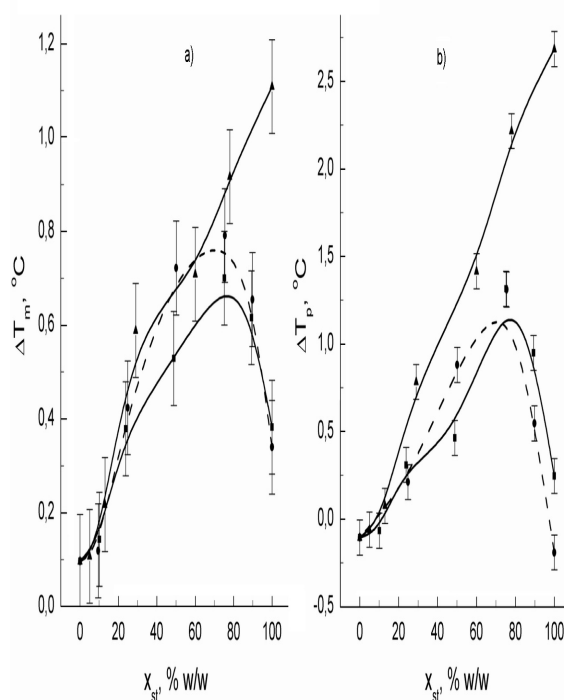

Fig. 4. Luminescence spectra of SrLa$_{4-x}$PrTi$_5$O$_{17}$ (x = 0.001) crystals; λ_{ex} = 78, 150 and 307 nm; T = 10 K.

125–185 nm. The region of 185–334 nm, apparently, is represented by the superposition of several bands forming a plateau with a total maximum in the vicinity of 270 nm. In contrast to the described above, the relative excitation intensity falls significantly in the first region in the spectrum of doped SrLa$_4$Ti$_5$O$_{17}$:Pr crystal. In addition, both the first and the second regions are structured. Four component with the peak positions at 68, 82, 92, 97 and 110 nm can be distinguished on the first region. Stronly overlapped peaks at 135, 160, and 190 nm can be distinguished on the other region (125–225 nm). UV region of the excitation spectrum (225–334 nm) for the doped sample looks like as an asymmetric band. The asymmetry of the band is probably due to increasing the relative excitation intensity in the longest wavelength part of the spectrum, if compared with the excitation spectrum of the wide PL band of the undoped sample. As a result, peak position of this region of the spectrum shifts to the long wave length side up to 307 nm.

Evaluation of the PL decay time is made within ~ 5–200 ns range of emission quenching. (Only this range is available for measurements of the PL kinetic at the "SU-
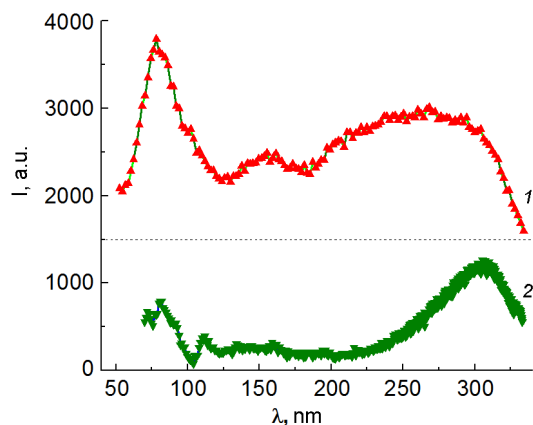
Fig. 5. Spectra of luminescence excitations of un-doped $SrLa_4Ti_5O_{17}$ (1) and doped $SrLa_{4-x}PrTi_5O_{17}$ ($x = 0.001$) crystals (2); $\lambda_{reg} = 530$ (1) and 610 nm (2); $T = 10$ K.

PERLUMI" station.) Time dependence of the luminescence quenching both of the wide band PL registered at the wave length of 495 nm for the un-doped crystal, and dopant luminescence measured on behavior of the maximal intensity line at ~ 610 nm for the doped $SrLa_4Ti_5O_{17}$:Pr sample, were measured at excitation with $\lambda_{ex} = 307$ nm. As it turned out, a decay of the wide short wave length PL band in the range of 30−200 ns is described by exponent with the decay time $\tau \approx 30$ ns. The emission near the PL line at 610 nm quenches substantially slower, thus, its intensity changes slightly for 200 ns after excitation light shut down. From this fact, we can conclude that the decay time of this quenching is not less than 5−10 μs.

The XRD data show that incorporation of dopant in amount of only 0.001 mol. % does not practically influence the $SrLa_4Ti_5O_{17}$ lattice parameters. Thus, representation about features of the $SrLa_4Ti_5O_{17}$ crystal structure (see Introduction) are completely applicable to the consideration of the $SrLa_4Ti_5O_{17}$:Pr crystal structure. It is obvious, that incorporation of praseodymium into the lattice of $SrLa_4Ti_5O_{17}$ compound is most probable in the form of Pr^{3+} ions on the positions of lanthanum, La^{3+}, ions. This type of incorporation is realized for many of oxide compounds containing lanthanum ions (see e.g., [18−20]). The conclusion follows from coincidence of radius of the Pr^{3+} and La^{3+} ions, those are in oxygen surround of lattice. In fact, radius of the Pr^{3+} is 1.179 Å and it is 1.216 Å for La^{3+} if the both ions are located in 9 oxygen atoms neighbourhood [21].

3.1 Undoped $SrLa_4Ti_5O_{17}$ luminescence.

Observed luminescence of the un-doped compounds is a pattern of intrinsic emission of the crystallophosfors. That is, the emission due to the processes of absorption of excitation quanta, the relaxation of the excitation energy and the radiation transitions in the intrinsic elements of the crystal lattice of the oxide matrix and its own defects. In fact, the excitation spectrum of the short (λ_{max} near 580 nm; ~ 2.14 eV) is quite wide, and its the most long wave length component is located at 4,13 eV (300 nm). So, the Stokes shift is very significant (1.99 eV), that is a clear indication that discussed luminescence is of "intrinsic" nature and this statement is consistent with the well-established approach (see, e.g., [22]).

Manifestation of the wide complex PL band and its dependences on the excitation wave length indicate that more than one luminescence center is involved in the luminescence processes. There were no previous information concerning luminescence of the $SrLa_4Ti_5O_{17}$ compounds, therefore, in discussing the possible nature of the observed emission we are based on the literature-known data about PL of similar in composition and structure materials. Obviously, in our case, first of all, one should consider the crystals of strontium titanate, $SrTiO_3$. As it has been mentioned in Introduction, the studied compounds consist of perovskite — like bloks, which similarly to strontium titanate contain jointed by vortex molecular groups of TiO_6 and Sr^{2+} ions. (It is common knowledge that La^{3+} ions are not active in luminescence, and therefore they should be considered only as modifiers of the crystalline field in which TiO_6 groups, Sr^{2+} ions and Pr^{3+} ion are located.) The data about value of the bandgap of any optical material, E_g, are very important for understanding the luminescence mechanisms in that material. There are no, of course, such data for $SrLa_4Ti_5O_{17}$ under study. As for strontium titanate, the single crystals of the materials are characterized with E_g values of ~ 3.7 and ~ 3.25 eV (335 and 381 nm) for direct and indirect bands, respectively. The absorption edge for $SrTiO_3$, formed the lowest band to band $2p(O^{2-}) \rightarrow 3d(Ti^{4+})$ transition, is evaluated by the value of 3.59 eV (28985 cm^{-1}, or 345 nm) [10, 23]. Taking into account the remoteness of the La^{3+} ions from the perovskite-like motives, we can assume that the E_g values, as well as absorption edge, for the $SrLa_4Ti_5O_{17}$ compounds

have also to be in the noted above ranges. Analysing the excitation spectra (Fig. 4), the absorption edge of the of $SrLa_4Ti_5O_{17}$ crystals can be estimated by the value of 3.51 eV (~ 28330 cm^{-1}, ~ 353 nm). It is easy to see, this value is close to the noted above concerning strontium titanate.

The $SrTiO_3$ crystals at the low temperatures and UV excitation show the wide structureless band of visible emission with the peak position near 500 nm [9, 10, 24, 25]. Calcium and barium titanates show the similar characteristics of the PL [8]. Mentioned intrinsic luminescence of the alkaline-earth titanates is ascribed to the emission of the self-trapped excitons (STE) of octahedral groups of TiO_6 [10, 13]. Taking into account the above noted similarity of the $SrTiO_3$ and $SrLa_4Ti_5O_{17}$ energy characteristics, we can suppose that the observed PL short-wave band is also due to the decay of excitons localized on the TiO_6 groups, for example, those, $Ti(3)O_6$, lying in the center of the perovskite-like blocks. The data about fast decay (≈ 30 ns) of the short wave length PL band agrees with this conclusion.

Origine of the long wave length IR luminescence component, due to the lack of data, can not be reliably determined. It can be ruled out that this PL is also associated with the decay of excitons localized on the groups $(TiO_6)^{8-}$, however, more distorced, that is, those that lie on the periphery of the mentioned perovskite-like blocks. At the same time, increasing intensity of the emission component with λ_{max} ~ 830 nm when excitation wave length also increases, indicates that this PL is better excited under the long wave length UV radiation. Therefore, there is a reason to take into account a participation of the lattice defects in this PL. That is, it is possible that this emission caused by decay of the molecular excitons of peripheral $(TiO_6)^{8-}$ groups localized on the lattice defects.

As is noted above the long wave length side of the PL spectra (900–1000–~1200 nm) rises, if λ_{ex} becames more than 300 nm. It is evidently, this enhancement is caused by appearance and further increasing the additional longer wave length IR luminescence band. So, this emission should be related with the second type of the peripheral $(TiO_6)^{8-}$ groups. However, it can not be excluded that this emission is caused by the luminescence centers, which are directly formed by defects of the lattice. It is obvious, the question of the origine of the observed bands of the $SrLa_4Ti_5O_{17}$ intrinsic luminescence needs further study.

3.2. Luminescence of the doped compounds.

Undoubtedly, the lines have been found in the PL spectra of compounds containing praseodymium, $SrLa_4Ti_5O_{17}$:Pr, are caused by the radiation transitions in impure Pr^{3+} ions located at positions of the lanthanum ions. Indeed, it is known from the literature, that Pr^{3+} ions are able to originate visible luminescence in four spectral regions, that lie in approximate ranges of 450–500, 520–550, 610–670 and 700–750 nm. The PL is determined by the electronic transitions from excited $^3P_1$, $^3P_0$, and $^1D_2$ levels to the Starks sub-levels of the lower lying energy multiplets ^3F_J and ^3H_J (see [26–29]) and mentioned above references too. The visible luminescence is caused by $^3P_0 \rightarrow {}^3H_4$, $^3H_5$ transitions (it can be range ≈485–515 nm (20500–19400 cm^{-1}), $^1D_2 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_6$ (the range ≈550–645 nm; ≈17000–5500 cm^{-1}), and $^1D_2 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3F_2$, $^3F_3$, $^3F_4$ (the ranges ≈650–690–740 nm; 15380–14500–13500 cm^{-1}). The view of measured by us emission spectra of $SrLa_4Ti_5O_{17}$:Pr in these ranges and the decay time (not less than 5–10 μs) correspond to numberous descriptions of the PL spectra and kinetics of Pr^{3+} in solids, and therefore we give the same explanation to the spectral details (see also notations in Fig. 4). More detailed interpretation of the lines in the Pr^{3+} spectra is always a complex task, and it should be emphasized that it is practically never solved unambiguously. The mentioned change in the ratio of the intensity of intrinsic and Pr^{3+} ions the PL depending on the excitation wave length, in our view, is caused by competition between excitation energy transfer processes, respectively, to the centers of their intrinsic luminescence and the PL centers formed by the praseodymium ions. This follows from the fact that in our experiments we did not deal with direct excitation of Pr^{3+} ions due to internal *f–f* transitions with the light absorption. In fact, the transitions from $^3H_4$ ground state to the active in luminescence $^1D_2$, $^3P_0$, $^3P_1$ excited states of the Pr^{3+} ions take place in the range of visible light absorption (≈470–610 nm; ≈21280–16390 cm^{-1}), and they are not realized in this work. The transitions to the higher energy lying $^1I_6$ and $^3P_2$ excited states take place with absorption in the range of ≈445–460 nm (≈22470–21740 cm^{-1}), that is also beyond of the spectral region used by us. The transitions only to the high energy $^1S_0$ state

provide absorption near ≈250 nm (≈40000 cm^{-1}) [29], that corresponds to the current in our studies excitation energy of PL. However, this absorption determines only a very narrow spectral range (~ 5–10 nm), and therefore it is not able to form the excitation spectrum in the range of 50–334 nm, in general. Thus, we can state that the excitation energy from the range of VUV and UV light (50–334 nm; 200000–59880 cm^{-1}) is delivered to the Pr^{3+} emission centers due to its transfer through the elements of $SrLa_4Ti_5O_{17}$ matrix. It is obvious, a that probability of the transfer should depend on the excitation quanta energy, since it determines by which elements of the lattice the energy is absorbed and the ways of its delivery to the emission centers and the specific energy states of the latter. Comparison of our data with the literature ones about various oxides contatining Pr^{3+} (see, e.g., [10, 18, 26–28]), shows that the radiation transitions from the $^3P_0$ level together with some contribution of the transition from $^1D_2$ level prevail in our case. So, we have to conclude that the transfer of excitation energy over the matrix and energy relaxation from the higher lying of the Pr^{3+} ions $^3P_2$ and $^3P_1$ states mainly lead to the population of these levels: $^3P_0$ and partially — $^1D_2$.

It seems, there is an exception from the noted above. That is manifestation of the short wave length luminescence band in the range of 330–450 nm (Fig. 4, curves *1*, *2*). This band, which does not manifest itself in the spectra of the un-doped crystals, can be associated with the allowed radiation $4f5d \rightarrow 4f$ transitions in the Pr^{3+} ions [14–16]. We have noted in Itroduction, that $4f5d \rightarrow 4f$ transitions are very attractive for scintillator deterctors needs, but we see, that their intensity is low. It is possible that for $SrLa_4Ti_5O_{17}$ crystals this result is due to the strong overlapping of the Pr^{3+} ions $5d$ levels with the conduction band of the matrix [14–16]. We hope that the perspectives for using the $5d$–$4f$ radiation of the studied materials will become clear after study of the $SrLa_4Ti_5O_{17}$ crystals of the higher concentrated by Pr^{3+} ions.

4. Conclusions

The results of luminescent study of the layered perovskite-like both undoped, $SrLa_4Ti_5O_{17}$, and doped with Pr^{3+} ions, $SrLa_4Ti_5O_{17}$:Pr^{3+}, compounds are reported firstly in this work.

Intrinsic luminescence of the $SrLa_4Ti_5O_{17}$ matrix is observed in 350–1100 nm range of the light wave lengths under excitation in the range of 50–334 nm at temperature of the samples 10 K. The spectrum of this luminescence is a superposition of luminscence bands with peak positions ~ 530, ~ 830, and ~ 1100 nm. The supposition is made that observed bands are caused by decay of excitons located on $(TiO_6)^{8-}$ molecular groups of three types, which differ by distorsion degree. The luminescence band at ~ 530 nm we have assosiated with the lowest distorsed groups that localized in the centre of the perovskite-like blocks of the $SrLa_4Ti_5O_{17}$ crystals. The bands near ~ 830 and ~ 1100 nm should be associated with more distorsed peripherical $(TiO_6)^{8-}$ octahedrons, which moreover are under effect of the lattice defects.

Doped with Pr^{3+} ions the $SrLa_4Ti_5O_{17}$ compound in addition to the mentioned intrinsic luminescence related with $4f \rightarrow 4f$ radiation transitions in the Pr^{3+} ions. Moreover, the low intensity band is observed in the range of 330–450 nm. This band is assotiated with $4f5d \rightarrow 4f$ transitions in the Pr^{3+} ions, we suppose.

The results of the work note the perspectiveness of $SrLa_{4-x}Pr_xTi_5O_{17}$ as well as similar perovskite-like titanate compounds elaboration as luminophores of wide emission spectrum.

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