Functional Materials 11, No.1 (2004)

Luminescent probes for some radioactive waste confinement phosphates

O.V.Chukova, R.S.Boyko, G.I.Gaididei, P.G.Nagornyi, S.G.Nedilko, I.M.Nedyelko, V.I.Radzivanov, V.P.Sakun, V.V.Boyko*

T.Shevchenko Kyiv National University, 2, block 1,
Acad.Glushkov Ave., 03680 Kyiv, Ukraine
*National Agricultural University, 8 Geroiv Oborony Str., Kyiv, Ukraine

Phosphate compounds are used for long time storage of many radioactive substances waste. For the first time the single crystals and glasses $NaTi_2(PO_4)$ compounds doped with rare-earth elements such as neodymium, samarium, dysprosium, praseodymium as well as indium ions have been obtained. Luminescence properties of the single crystals were investigated at 4.2, 77, and 300 K temperatures. It was shown that the luminescence spectra are superposition of the wide band of the proper "red" luminescence band of the $NaTi_2(PO_4)_3$ matrix emission and linear spectra caused by intrinsic transitions in *f*-shells of the impurity rare-earth ions. The "red" luminescence is considered as a result of emission of Ti^{3+} ions spontaneously formed in the $NaTi_2(PO_4)_3$ matrix. Analysis of the fine structure of the spectra shows that indium, samarium, and dysprosium impurities are arranged into the $NaTi_2(PO_4)_3$ matrix as the In^{3+}, Sm^{3+} and Dy^{3+} ions.

Соединения фосфатов используются для долгосрочного хранения многих радиоактивных отходов. Впервые получены монокристаллы и стекла $NaTi_2(PO_4)_3$, легированные примесями редкоземельных элементов, таких как неодим, самарий, диспрозий, празеодим, а также ионами индия. Исследованы люминесцентные свойства монокристаллов при температурах 4.2, 77 и 300 K. Показано, что спектры люминесценции являются суперпозицией широкой полосы собственной красной люминесценции матрицы $NaTi_2(PO_4)_3$ и линейчастых спектров, вызванных внутренними переходами в *f*-оболочках примесных редкоземельных ионов. "Красная" люминесценция рассматривается как результат переходов в ионах Ti^{3+}, которые спонтанно формируются в матрице $NaTi_2(PO_4)_3$. Анализ тонкой структуры спектров показал, что примеси индия, самария и диспрозия входят в матрицу $NaTi_2(PO_4)_3$ в виде ионов In^{3+}, Sm^{3+I} и Dy^{3+}.

The forms for radioactive waste confinement must be stable for geologic time scales (~10^6 years) and retain radioactive elements in their matrix without going away to the environment. Unfortunately physical and chemical properties of the waste containing materials are altered by internal radiation and as a result their structure can be destroyed. In order to monitor a state of the waste forms we have started investigation of some suitable waste host matrixes using luminescent probes such as ions of the rare earth elements (RE). A possibility of application the luminescence centers formed by impurity ions at their non-isomorphic and in particularly non-isocharged insertion into matrix for control of its state is based on the fact that peculiarities of the structure of such centers and electron-vibration interactions in them are caused in general by the nearest surrounding of the impurity, but not by the structure of "ideal" zero-defect matrix.

This paper presents the preliminary results of luminescence investigation of perspective materials for confinement of fission products and radioactive compounds such as phosphate compounds $MTi_2(PO_4)_3$

doped with the RE = Nd, Pr, Sm, Dy, and In ions as well.

Interest to ions of the RE elements is attracted by the fact that such ions are characterized by discrete linear luminescence spectra at various conditions. The spectra are caused by the inner *f-f* transitions within f^n shell [1–3]. Possibility to choose among the RE ions in lanthanide row the different ions with emission spectra in a wide spectral region (from ultraviolet to infrared) make promising usage of these impurities as a luminescent probe for investigation of crystals including the $NaTi_2(PO_4)_3$ crystals.

It must be noted that information about arrangement of the RE ions into the $NaTi_2(PO_4)_3$ matrix should give a confirmation of allocation of radioactive elements ions in these matrices. Especially it may concerns to actinide ions because their crystallochemistry properties are similar with ones of the RE ions.

Crystalline and glass samples of the $NaTi_2(PO_4)_3$ sodium titanium ortophosphate were synthesized from a melt of Na_2O, P_2O_5, and TiO_2 oxides composition. Study of the phase states of solidification products of the $Na_2O–P_2O_5–TiO_2$ system have shown the $NaTi_2(PO_4)_3$ compound is formed within a range of mole ratio Na_2O/P_2O_5 from 1:1.3 up to 1.45:1. The optimal ratio 1.2:1 between Na_2O and P_2O_5 was found after series of experiments. The content of the TiO_2 oxide in the melt was equal to 17 mass %, the RE elements contents were up to 1 mass % with respect to oxides. The $NaPO_3$ and $Na_4P_2O_7$ ("chemically pure for analysis" qualification) salts as well as the TiO_2 ("especially pure" qualification) Sm_2O_3, $Dy(NO_3)_3{\cdot}6H_2O$, and In_2O_3 ("chemically pure" qualification) oxides were used for synthesis.

Platinum crucibles with the noted oxides were placed into a high-temperature furnace at the $T = 1100°C$ and were being kept at this temperature during 14–17 h. Then the melt was being cooled with a rate 5 degree per hour up to 800°C that led to prevent spontaneous crystallization. After finishing the crystallization process at 800°C, the rest of liquid phase was poured off and converted into amorphous glass-like samples. Then the crystalline samples were cooled in the furnace up to the room temperature. Further, they were washed from amorphous phase firstly with dilute solutions of mineral acids HNO_3 and H_2SO_4, then with distillate water and pure alcohol. After all, they were dried. The obtained crystalline samples had the dimensions about 3×5×8 mm^3. The glass samples sizes was about 10×10×10 mm^3.

Table 1. Coordinates of basic atoms for the $NaTi_2(PO_4)_3$ compound

Atom	**x/a**	**y/b**	**z/c**
Na	0	0	0
Ti	0	0	0.14514(1)
P	0.71236(4)	0	0.25
O_1	0.1741(1)	0.1972(1)	0.30735(4)
O_2	0.4756(1)	0.3059(1)	0.25496(3)

X-ray diffracton phase analysis showed that the composition of the spontaneously formed crystals corresponds to the $NaTi_2(PO_4)_3$ compound. It is well-known that the $NaTi_2(PO_4)_3$ crystals are characterized by the rhombohedral cell with the parameters **a** = 8.502(5) and **c** = 21.833(9) Å ($\mathbf{a}_{rh}$ = 8.775 Å , δ_{rh} = 57°56′) [4]. The coordinates of the lattice basic atoms are presented in Table 1.

In the $NaTi_2(PO_4)_3$ crystalline structure the sodium cations are located at the centers of inversion and are surrounded by 6 atoms of oxygen that forms a prolonged octahedron: its lateral edges are enlarged up to 3.745 Å in comparison with other ones which are equal to 2.634 Å in the tops being common with two Ti-octahedrons of more perfect configuration (an average distance Ti–O = 2.002 Å). Atoms of phosphorus are located in the middle of the oxygen P-tetrahedrons formed by 4 oxygen atoms. These isolated P-tetrahedrons have usual for the P–O and O–O bonds distances: 1.530–1.532 and 2.461–5.527 Å respectively. Various interatomic distances for investigated structural units in the $NaTi_2(PO_4)_3$ crystal lattice are presented in Table 2.

The base of the $NaTi_2(PO_4)_3$ structure consists of the triplets of octahedrons (Ti–Na–Ti) stretched along a long axis **c**. These octahedrons have a common basis. The discrete triplets ($NaTi_2O_{12}$) integrates via the fourth empty octahedrons into an infinite chain along the rotoflection axis of the 3rd order (it is the only one such axis in the rhombohedral cell).There are three such axes at heights *h0*, 1/3, 2/3 in an ordinary double centered hexagonal cell. The PO_4 orthotetrahedrons are attached to the edges of an empty octahedron. Via the others two vertex the PO_4-tetrahedrons can connect with neighboring columns. So, there are two triplets of Ti–Na–Ti octahedrons with two

Table 2. Interatomic distances (in) for $NaTi_2(PO_4)_3$ compound

Na-octahedron	Ti-octahedron	P-tetrahedron
a-O_2 (6) 2.289(1)	Ti–O_1 (3) 1.896(1)	P–O_1 (2) 1.532(1)
O_2–O_2' (6) 3.745(1)	Ti–O_2 (3) 2.107(1)	P–O_2 (2) 1.530(1)
O_2–O_2'' (6) 2.634(1)	Average Ti–O:2.002	Average P–O:1.531
Average O_2–O_2:3.190	O_1–O_1' (3) 2.749(1)	O_1–O_1' (2) 2.527(1)
	O_2 (3) 2.778(1)	O_2 (2) 2.522(1)
	O_2' (3) 3.115(1)	O_2' (2) 2.461(1)
	O_2–O_2' (3) 2.634(1)	O_2–O_2' (2) 2.508(1)
	Average:2.819	Average:2.504

triplets of the PO_4-tetrahedrons between them in the unit's period along **c**-axis. They are connected by two triplets of double horizontal axes and three vertical glide planes, which intersect these axes. The rotoflection axis turns the PO_4 triplets' one with respect to other for 60° that can be seen at the end projection of this structure [4].

Luminescence spectra of the $NaTi_2(PO_4)_3$-samples were obtained at 4.2, 77 and 300 K. At low temperatures (4.2 and 77 K) the samples were placed into helium (nitrogen) cryostat with liquid helium (nitrogen). The ILGI-501 laser radiation (λ = 337.1 nm) and DRSh-250 mercury lamp radiation were used for excitation of photoluminescence (PL). Radiation of mercury lamp was filtered by a number of glass and liquid filters that gave a possibility to separate from the line spectrum a set of lines in the range 250–380 nm or some lines from the same range. The DFS-12 spectrometer was used for registration of luminescence spectra. The spectra on Fig.1–3 are given without correction on a spectral sensitivity of the equipment.

Estimation of decay time of PL was made on the base of studying the kinetics of luminescence decay that was registered by photomultiplier in a time strobbing regime with using for excitation the ILGI-501 laser (pulse generation duration is about 8–10 ns) [5]. The method of investigation of kinetics of the X-ray luminescence (XL) decay was described formerly [6].

The $NaTi_2(PO_4)_3$ undoped crystals reveals intensive emission at the light excitation in a range 250–380 nm for λ_{ex} (40000–26300 cm^{-1} for ν_{ex}). Luminescence spectra consists of two bands: the short-wave luminescence band (LB-I) in a range 460–700 nm with a maximum position at about ~545 nm and the long-wave luminescence band (LB-II) in a range 720–800 nm with a maximum position at $\lambda_m \cong$765 nm (Fig. 1).

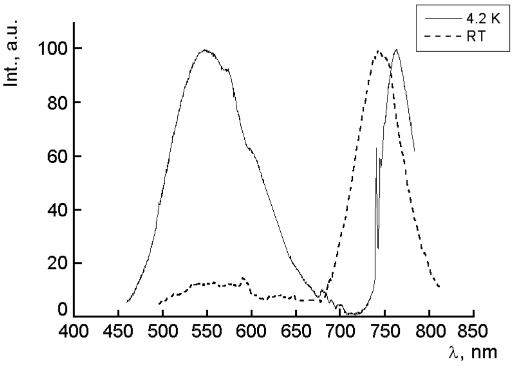

Fig. 1. Luminescence spectra of the $NaTi_2(PO_4)_3$ undoped crystals, λ_{ex} = 337.1 nm.

The LB-II band consists of several components while the LB-I band is practically structureless excepting two shoulders of small intensity which are observed in the ranges 570–585 and 595–625 nm. The LB-II band consists of wide unstructured component with $\lambda_m \cong$ 765 nm and two sharp peaks at $\lambda_m \cong$ 740 nm, and $\lambda_m \cong$ 745 nm, and a weak shoulder at $\lambda_m \cong$ 750 nm on its short-wave wing (Fig. 1).

One can observe some additional details like a set of narrow lines in the PL spectra of the samples doped with the RE-ions in addition to considered bands and peaks of undoped crystals. Number of series, their spectral location, number of lines in the series and their position depend on a type of the impurity.

Thus, in the photoluminescence spectra of the samples doped with the Sm^{3+} ions (the $NaTi_2(PO_4)_3$ (Sm) crystals) three series of additional lines are observed in the range 520–580, 590–630, and 650–695 nm (Fig. 2).

The Dy-doped crystals reveal emission with additional lines observed in the ranges

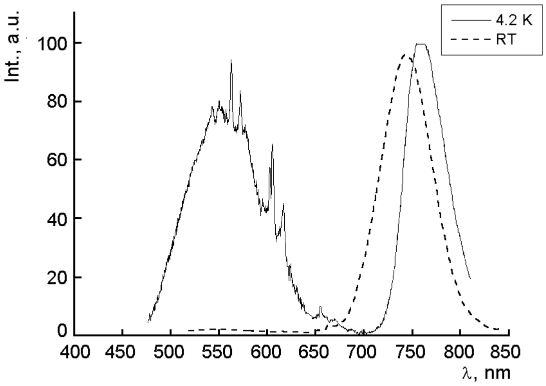

Fig. 2. Luminescence spectra of the $NaTi_2(PO_4)_3$ crystals doped with the Sm^{3+} ions, λ_{ex} = 337.1 nm.

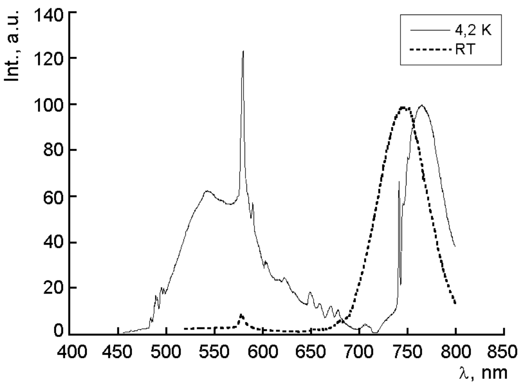

Fig. 3. Luminescence spectra of the $NaTi_2(PO_4)_3$ crystals doped with the Dy^{3+} ions, λ_{ex} = 337.1 nm.

Table 3. Decay time (ns) of the X-rays luminescence for the doped samples $NaTi_2(PO_4)_3$ at room temperature

Impurity	Decay components, ns		
	τ_1	τ_2	τ_3
In	6.6	61	
Nd	7±1	100±10	1176
Pr	7.4±1	90±10	1238
Sm	6.8	63	
Dy	6.3	47	

of 425–500, 560–620, and 635–720 nm (Fig. 3). The LB-II band of the $NaTi_2(PO_4)_3$ (Dy) crystals like to the case of pure crystals consists of wide unstructured component with $\lambda_m \cong 765$ nm with two sharp peaks at $\lambda_m \cong 741$ nm and not so intensive peaks at $\lambda_m \cong 746$ nm and at $\lambda_m \cong 750$ nm on its short-wave wing. A shoulder at 722–730 nm was observed as well (Fig. 3).

Adding of the indium ion impurities cause only a strong decreasing of intensity of the LB-II band.

Increasing of temperature from 4.2 K to room temperature causes redistribution of intensities of spectral components. Relative intensity of the LB-I band strongly decreases with increasing of temperature. Maximum position of the LB-II band shifts from $\lambda_m \cong 765$ nm on $\lambda_m \cong 745$ nm. No sharp peaks were observed on the short-wave wing of the LB-II band at room temperature. Narrow spectral lines of the RE doped crystals were not observed at room temperature ether. As to kinetics of luminescence, it is worth to note that at first kinetics decay was registered in the integrated spectral regime: the total luminescence emission fell into the photo-multiplier cathode. The PL decay curve is rather complicated: it consists of the fast component (we could not estimate its duration) and slow component with an effective decay time = 5÷25 μs which depends on the type of impurity and temperature of the samples.

Decay time for the fast components was estimated according to results of measuring kinetics of the X-rays luminescence decay because at this case an excitation of emission was effected by essentially shorter pulses with duration about 1–2 ns. As for the case of the PL decay, the XL decay also has complicated character. There are the components with the decay time of 10 ns and 100–200 ns as well as the components with $\tau \approx 1$ μs and $\tau >> 1$ μs (unfortunately we could not obtain more precise values for two last components). All data is presented in Table 3.

The data on the linear luminescence spectra of the crystals doped with the RE ions is simplest for analysis. Observed peak positions and numbers of spectral lines for these crystals agree with data on luminescent properties of the triple-charged RE ions. These lines are caused by intrinsic radiation transitions in the $4f^n$-shells of the RE ions [1–3].

The present data on spectroscopy of the RE ions enables to assign the observed linear PL spectra of the investigated Sm^{3+}-doped crystals to inner transitions in the Sm^{3+} ion [7]. Three groups of narrow spectral lines observed in the PL spectra are caused by the radiation transitions from the actual in luminescence excited level $^4G_{5/2}$ on three lowest states of a ^6H manifold: $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ [6, 7]. The Sm^{3+}

ions have an odd number of electrons and twice Kramer's degeneration of these ions in crystal field is actual. It means that corresponded spectral regions have to contain 3, 4, and 5 spectral lines for J equal 5/2, 7/2, and 9/2, respectively. Therefore, the observed series of additional lines in the 520–580, 590–630, and 650–695 nm spectral regions (Fig. 2) are corresponded respectively to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ electron transitions in the $4f^n$-shells of the Sm^{3+} ions.

At the same manner, the groups of narrow spectral lines observed in the PL spectra of the Dy-doped crystals can be assigned to the electron transitions in the $4f^n$-shells of the Dy^{3+} ions. The lines of the most long wave length region, obviously, assigns to the $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition, group in the 560–610 nm spectral region is connected with the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, and short wave length region is an exhibition of the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition [3]. Remind, at the whole removal of degeneration at crystal field (taking into account double Kramer's degeneration) the number of lines for transition from one manifold of the $^4F_{9/2}$ level to the $^6H_{11/2}$, $^6H_{13/2}$, $^6H_{15/2}$ levels have weather to be equal 6, 7, and 8, respectively. A number of lines observed in the noted spectral regions for both considered impurity ions are corresponded to the noted number of levels [1–3, 7, 8]. It evidence about whole cancellation of degeneration in the crystal field. This conclusion agrees with the most probable arrangement of the impurity RE ions in the crystal lattice: the RE ions replace the titanium ions. Comparison of ionic radii of the Sm^{3+} and Dy^{3+} ions with ionic radius of the Ti^{4+} ions and Ti–O distance (Table 2) follows possibility of such replacement.

At the same time it must be noted that exceed charge −1 arises. Its possible local compensation can occur by formation of oxygen vacancy or by placement of some ions near the RE ion. In the both cases symmetry of the RE luminescence center must be low (probably C_1), but not octahedral. Even this fact causes cancellation of degeneration of the levels.

As to the wide band and the details of the fine structure of the "red" luminescence, this luminescence is to be corresponded to the proper matrix emission because the same luminescent bands are observed for undoped samples. In contrast to the results of consideration the "blue-green" luminescent band, one can make some definite assumptions about a character of this radiation. For the moment, it can be done only by comparing its characteristics with luminescent data of compounds doped by titanium ions. Analysis of the literature data showed that emission bands of the impurity titanium ions embedded into oxide dielectric matrices are located in this spectral diapason 600–900 nm [9, 10].

The ionic radius of the Ti^{3+} titanium ions is equal to 0.67 Å. They can replace the Ti^{4+} titanium ions Ti^{4+} in a lattice (the ionic radius is 0.64Å), in the assumption of uncontrolled formation in the matrix of the triple-charged titanium ions. In the synthesized samples, the Ti^{3+} ions can be formed under the process of high-temperature synthesis and spontaneous uncontrolled transition from melt into solid state at cooling.

There is one electron in the external $3d$-shell of the titanium ions Ti^{3+}. An electron state is described by ^2D-term. In crystalline field of cubic symmetry, this term is splitted into two levels $^2T_{2g}$ and ^2E_g with a splitting amount about 18000–19000 cm^{-1}. At further symmetry lowering and because of spin-orbital interaction a lower level is resolved into two and three levels respectively with a total splitting amount about 100 cm^{-1}. The upper level ^2E_g is also resolved into two sublevels due to Jahn-Teller effect. The splitting amount is about 2000 cm^{-1}. Radiation transitions $^2E_g \rightarrow {}^2T_{2g}$ are forbidden in accordance with evenness low but in crystalline field of low symmetry this forbiddance is canceled. As a result lifetime of the Ti^{3+}-ions in the ^2E_g-state is about 1–3 μs. As for other ions in the Fe-group an external electron at T-states strongly interacts with the lattice vibrations. Therefore luminescence bands may be rather wide that is observed in a number of experiments: they are located in a range 650–1200 nm.

Taking into account the described properties of the Ti^{3+}-ions energetic it is easy to understand that optical transitions from the lower level of the excited state ^2E_g to the ^2A and ^2E levels of the ground state may cause the wide band of the "red" luminescence as well as details of the fine structure being observed experimentally in the luminescence spectra of the $NaTi_2(PO_4)_3$ compound.

Described above results allow us to do the follow conclusions.

1. For the first time compounds of the $NaTi_2(PO_4)_3$ compositions doped with the rare-earth elements such as samarium, dysprosium, praseodymium as well as indium

ions have been synthesized and their samples in the form of single crystals and glass are obtained. It is shown that the both doped and the "pure" $NaTi_2(PO_4)_3$ crystals have the PL and XL spectra.

2. Luminescence spectra of the noted single crystals are investigated at 4.2 and 300 K.

3. Luminescence of the $NaTi_2(PO_4)_3$ crystals doped with the RE ions Pr^{3+}, Sm^{3+} and Dy^{3+} is excited both in the impurity-absorbing region and the matrix-absorbing region.

4. Luminescence spectra of undoped crystals consist of two bands: short-wave one (450–700 nm) of still unknown origin and long-wave one (720–800 nm) most likely caused by the Ti^{3+}-ions luminescence (these ions can be formed spontaneously).

5. It is shown that the luminescence spectra represent a superposition of unstructured wide band of the own "red" luminescence of the $NaTi_2(PO_4)_3$ matrix and fine-structured line spectra caused by transitions in the intrinsic $4f$-shells of the impurity rare-earth ions (Fig. 2, 3).

6. The "red" luminescence may result from the emission of Ti^{3+} ions in $NaTi_2(PO_4)_3$ matrixes. Indium ions impurities cause a strong decreasing of intensity of the matrix "red" own luminescence.

7. Analysis of the spectra fine structure shows unambiguously that samarium, dysprosium and praseodymium impurities are incorporated into the $NaTi_2(PO_4)_3$ matrix as the Sm^{3+}, Dy^{3+} and Pr^{3+} ions replacing the Ti^{4+}-ions.

8. A possibility of such substitution indicates the fact that tetra-charged ions of radioactive elements also can be embedded into the $NaTi_2(PO_4)_3$ compound matrix. So such a matrix can be used for conservation of radioactive wastes.

Acknowledgments. The authors are appreciated to the head of the experimental physics chair of I.Franko National University Prof.A.S.Voloshinovski and his collaborators for measuring the X-rays luminescence characteristics.

References

1. A.A.Kaminskii, U.Hommerich, D.Temple et al., *Phys. Stat. Sol.(a)*, **174**, R7 (1999).
2. S.Hufner, Optical Spectroscopy of Lanthanide in Crystalline Matrixes. Systematic and Properties of the Lanthanide, D.Reidel Publishing, New York (1983).
3. S.G.Nedilko, O.V.Chukova, M.Diab, V.I.Sheludko, *Functional Materials*, **7**, 450 (2000).
4. Yu.A.Ivanov, E.L.Belokoneva, Yu.K Egorov-Tismenko et al., *Dokladi AN SSSR*, **252**, 1122 (1980).
5. I.Ya.Kushnirenko, V.P.Sakun, *Proc. Kyiv University (Physics)*, **22**, 24 (1981).
6. A.S.Voloshinovskyi, A.G.Dmitrijev, V.B.Mikhailik, P.A.Rodnyi, *Fiz. Tverd. Tela*, 34, 3730 (1992).
7. M.J.Treadaway, R.C.Powell, *Phys. Rev. B.*, **11**, 862 (1975).
8. O.Chukova, S.Nedilko, Z.Moroz, M.Pashkovskyi, *J. Luminescence*, **102–103**, 498 (2003).
9. A.O.Matkovskyy, Materials for Quantum Electronics, Liga-Press, L_i (2000).
10. F.Bantien, P.Albers, G.Huber, *J. Luminescence*, **36**, 363 (1987).

Люмінесцентні проби для деяких фосфатів, що придатні для зберігання радіоактивних відходів

О.В.Чукова, Р.С.Бойко, Г.І.Гайдідей,
П.Г.Нагорний, С.Г.Неділько, І.М.Недєлько,
В.І.Радзіванов, В.П.Сакун, В.В.Бойко

Сполуки фосфатів використовуються для довгострокового зберігання багатьох радіоактивних відходів. Вперше одержано монокристали і стекла $NaTi_2(PO_4)_3$, леговані домішками рідкісноземельних елементів таких, як неодим, самарій, диспрозій, празеодим, а також іонами індію. Досліджено люмінесцентні властивості монокристалів при температурах 4.2, 77 і 300 К. Показано, що спектри люмінесценції є суперпозицією широкої смуги власної червоної люмінесценції матриці $NaTi_2(PO_4)_3$ та лінійчатих спектрів, спричинених внутрішніми переходами в f-оболонках домішкових рідкісноземельних іонів. "Червона" люмінесценція розглядається як результат переходів в іонах Ti^{3+}, що спонтанно формуються у матриці $NaTi_2(PO_4)_3$. Аналіз тонкої структури спектрів показав, що домішки індію, самарію та диспрозію входять у матрицю $NaTi_2(PO_4)_3$ у вигляді іонів In^{3+}, Sm^{3+} і Dy^{3+}.