

Radiation stability of co-doped NaI:Tl scintillators

N. Shiran, A. Gektin, E. Galenin, S. Vasyukov, V. Nesterkina

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine, 60 Nauky Ave., 61001 Kharkiv,
Ukraine

Received March 12, 2019

It is shown that there are potential hidden mechanisms that can deteriorate the radiation stability of NaI(Tl) scintillators. It turned out that the formation of intrinsic hole centers upon irradiation is not the main reason for the decrease in scintillation yield, but their role increases in case of codoping. The determining process is the capture of carriers directly by thallium ions with the conversion of Tl^+ to Tl^{2+} . As a result, a positive effect of codoping can be achieved only with a strictly specified balance between these mechanisms.

Keywords: radiation stability scintillators, hole centers, codoping crystals

Показано, что существуют потенциальные скрытые механизмы, влияющие на радиационную стойкость сцинтилляторов NaI(Tl). Оказалось, что образование собственных дырочных центров при облучении не является основной причиной уменьшения выхода сцинтилляций, однако их роль возрастает в содопированных кристаллах. Определяющим фактором является процесс захвата носителей непосредственно ионами таллия с превращением Tl^+ в Tl^{2+} . В результате положительный эффект от содопирования может быть достигнут только при строго определенном балансе между этими механизмами.

Радіаційна стійкість содопованих сцинтиляторів NaI:Tl. *Н.Ширан, А.Гектін, Е.Галенін, С.Васюков, В.Нестеркіна*

Показано, що існують різні механізми, що впливають на радіаційну стійкість сцинтиляторів NaI(Tl). Виявилось, що утворення власних диркових центрів при опроміненні не є основною причиною зменшення виходу сцинтиляцій, проте їх роль зростає у содопованих кристалах. Визначальним фактором є процес захоплення носіїв безпосередньо іонами талію з перетворенням Tl^+ у Tl^{2+} . У результаті позитивний ефект від содопування може бути досягнутий тільки при строго певному балансі між цими механізмами.

1. Introduction

One of the last year trends in alkali halide crystals modification connects with the use of the co-doping technique. Typical example of this approach is improving the scintillators parameters of the NaI(Tl) [1, 2]. Despite the 70-year history of the development and application of this material, some improvement in the scintillator performance

takes place, although there is no understanding of this phenomenon.

Even the well-known improvements of NaI scintillation parameters due to co-doping of crystals with Ca or Sr ions do not have a clear description. Accordingly, there are no ideas on the limits of possibilities of this method as applied to NaI(Tl). No one has investigated what happens with absorption and luminescence of activated NaI(Tl, Ca) in weakly irradiated (UV <320 nm)

crystals. There is no clear understanding of the main changes in the optical properties of crystals upon doping with divalent ions. High hygroscopicity of NaI inevitably leads to contamination by oxygen-containing impurities, which, ultimately, leads to a deterioration of their scintillation parameters [3–5]. A priori can be assumed that the main ways are either the purification of the melt as a result of the scavenger action or the change in the structure of activating centers as a result of interaction with co-dopant ions.

However, the study of co-doped NaI(Tl) crystals is at the beginning. In particular, we can assume that the introduction of Me^{2+} ions into the crystal lattice can affect not only the solid-state properties of the crystal, but also to the energy transfer to the activator centers. The latter can affect the absorption and luminescent of crystals [6].

It should be noted that the excess charge of Me^{2+} ions is compensated by cationic vacancies and/or oxygen ions, which leads to the creation of single dipoles $\text{Me}^{2+}\text{V}_c^-$ and/or $\text{Me}^{2+}\text{O}^{2-}$, their aggregates and precipitates. The appearance of excess cation vacancies stimulates the appearance of V type centers (l_3^- , l_2^- , l_n), which are stable at room temperature [7–11]. It can be expected that scintillation yield may decrease in co-doped NaI(Tl) crystals, as well as increase the afterglow and rising up the radiation sensitivity. However, the nature of such phenomena has not yet been studied in co-doped NaI(Tl) crystals.

This work is devoted to the study of the dominant mechanisms of NaI(Tl) properties change as a result of co-doping with divalent cations.

2. Experimental

Crystals of non-activated NaI, activated crystals of NaI(Tl), NaI(Ca), NaI(Eu) and co-doped crystals of NaI(Tl,Ca) and NaI(Tl,Ca,Eu) were grown by the Bridgeman-Stockbarger method or continues CZ technique in vacuum or controlled reactive atmosphere. Concentration of Tl^+ , Eu^{2+} and Ca^{2+} in melt was about 0.1 mol %. Dopant contain in the crystals was determined by chemical methods or/and absorption spectroscopy. Measurements of absorption, emission, and excitation spectra were performed as at [4, 5]. The absorption spectra of crystals were measured by SPECORD 40 spectrophotometer. Emission spectra were studied by FLS'920 fluorescence spectrometer. A Xe900 steady state xenon lamp was used for UV spectroscopy. Radiation coloration of samples was realized by UV- and X-ray irra-

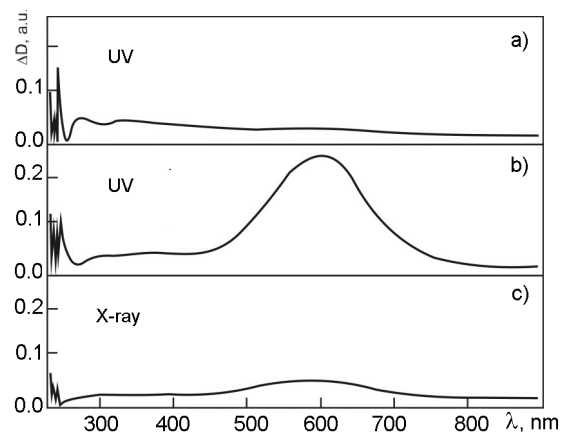


Fig. 1. UV- and X-ray induced absorption spectra of NaI crystals with different purity.

diation (tube Cu, 10 mA, 40 kV, 1.0 R/min). Due to the high hygroscopicity of NaI, we used only the encapsulated crystals.

The scintillation parameters were measured for ^{137}Cs source. Spectra measurements were performed using standard analogue approach at MCA, model Multiport II (Canberra) with standard Hammamatsu PMT HM R1307.

3. Results and discussion

3.1 NaI pure

For comparison, nominally pure NaI crystals, NaI(Ca), NaI(Tl,Ca) and NaI(Tl,Ca,Eu) crystals were studied. In this work all crystals were grown from the same raw material and technology. It has to be noted that non-doped NaI crystal are always nominally pure. Such crystals demonstrate significantly different optical, luminescence and scintillation characteristics [4, 11–14]. It is well known that the radiation sensitivity of crystals is a determining criterion for their purity [4, 13, 14]. The optical absorption spectra of irradiated pure crystals are shown in Fig. 1. The shapes of curves are similar for both X-ray and UV irradiation, but the difference between the distinct crystals are clearly marked. Oxygen or hydroxyl trace initiates appearance of F-centers (590 nm) and V-centers (290–370 nm). The presence of F-centers indicates the contamination by hydroxyl (OH^-) and hydrogen (H^-) ions, which absorption lies in the 240–260 nm range. The conversion of such ions into F-centers under irradiation is the reason for coloration. Thus, the mechanism of color centers' generation in pure NaI scintillators connects with uncontrolled impurities. The lack of such peaks is one of the main criteria for crystals selection for this study.

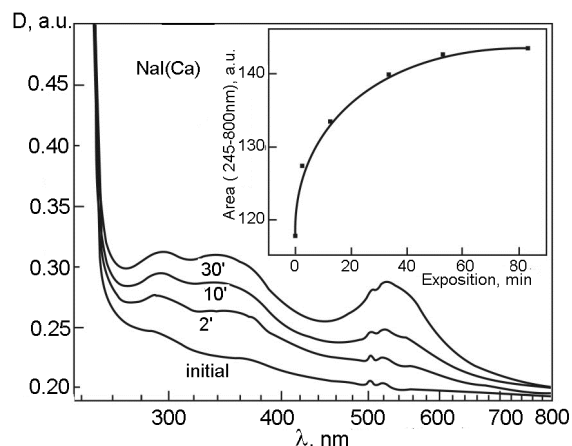


Fig. 2. Optical density of initial and UV-irradiated NaI(Ca) crystal. Inset: kinetics of the color centers accumulation.

3.2 NaI(Ca)

The absorption spectra of the initial NaI(Ca) and nominally pure NaI crystals are almost the same. However, a series of intense peaks at 296, 360, 540 nm appear in absorption spectra of NaI(Ca) crystals. Peaks are rise up with exposure dose increase (Fig. 2). The typical spectrum of UV-induced absorption of NaI(Ca) crystal is shown in Fig. 3. The bands appearing in the 290–400 nm range are associated with V-centers are associated with V centers that are stable at room temperatures only in additively colored alkali halide crystals. Thus, UV irradiation induces color centers in NaI(Ca). The similar absorption bands were found in NaI with excess iodine.

Study of V-type centers in alkali iodide crystals doped with divalent cations revealed that of Ca^{2+} ions presence leads to hole centers stabilization [7–10]. Resonant Raman scattering allows to determine the nature of stable V centers created under X or γ irradiation in alkali halides. At early stage of irradiation at low temperature, trihalide ions I_3^- are formed. By increasing the radiation dose, polyhalide ions, characterized by the vibrational mode of the halogen molecule in I_n^- ($n = 5\dots$) appear. These centers are precursors of halogen clusters created at room temperature. Thermal annealing almost restores the crystal except for voids, which remain after the disappearance of halogen aggregates. The stabilization of halogen interstitials into V centers is the major process for production of stable electron and hole defects obtained in alkali

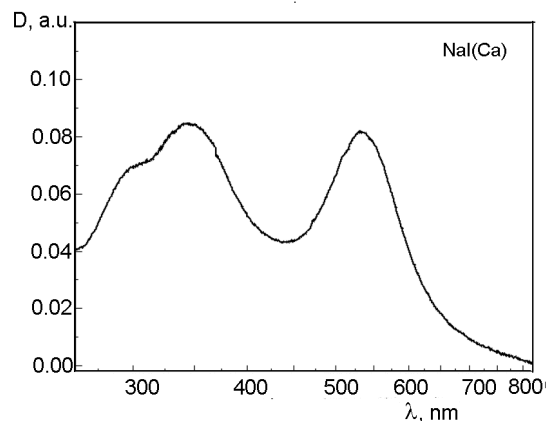


Fig. 3. UV-induced absorption spectra of NaI(Ca) crystal.

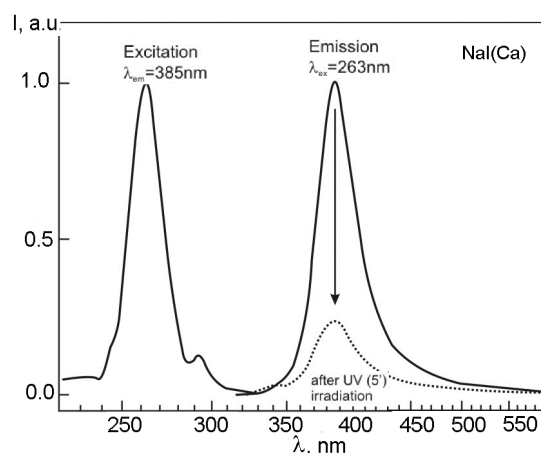


Fig. 4. Excitation and luminescence spectra of NaI(Ca) crystal. Dotted curve demonstrates the suppression of emission after 5 min of UV-irradiation.

halide crystals exposed to ionizing radiations [10].

The photoluminescence spectrum of NaI(Ca) shows a band with a maximum near 386 nm (Fig. 4). This emission is excited at the tail of fundamental absorption. This luminescence is caused by $\text{Ca}^{2+}\text{V}_c^-$ dipoles. Short UV (as well as X-ray) exposure leads to a rough quenching of this emission. The suppression of luminescence is obviously associated with the appearance of V-centers, absorbing in this range as can be seen from Fig. 3.

Based on the general concepts, the introduction of a calcium ion commensurate with the sodium ion into NaI is accompanied by the formation of single dipoles ($\text{Me}^{2+}\text{V}_c^-$), di-vacancies, and their aggregates.

Luminescent properties of NaI(Ca) crystals are not described in the literature. By analogy with other alkali metal iodides (in

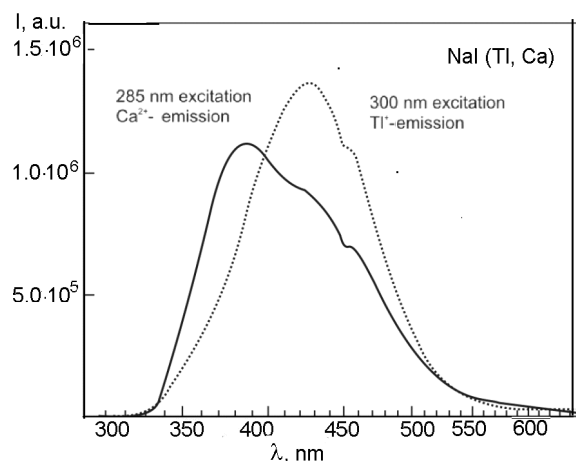


Fig. 5. Luminescence spectra of NaI(Tl,Ca) crystal excited in bands typical for Tl^+ and Ca^{2+} ions (300 and 285 nm, respectively).

particular with CsI(Ca) crystals) the luminescence can be associated with the so-called "indirect luminescence", i.e. with localization of excitons on defects such as dipoles ($Ca^{2+}V_C^-$). Introduction of calcium into alkali iodides leads to stabilization of the hole color centers J_3^- and $(I_2^-)_n$ type [9, 10]. Probably, calcium in NaI(Ca) can bind hydroxyl and oxygen, playing the role of scavenger, similarly to doping CsI crystals by europium (Eu^{2+}) [15]. It was demonstrated for CsBr(Eu) as well [16].

A similar luminescence (~ 375 nm) were found in NaI crystals grown in excess of iodine atmosphere [11, 12]. Since centers are created by additive stay in iodine vapor and do not occur when stay in sodium vapor, they are classified as hole traps of V centers type.

Comparing the differences in the optical properties of pure NaI (Fig. 1) and Ca-containing NaI crystals (Figs. 2 and 3), we have to take into account that the absorption band near 240 nm is hypothetically associated with OH^- or H^- ions. $OH^- \rightarrow U$ reaction takes place with the subsequent conversion of U centers to F-centers and oxygen ions (O^{2-}) under UV irradiation of hydroxyl containing crystals [4, 14].

3.3 NaI(Tl,Ca)

A priori, the role of calcium ions in change of NaI(Tl) properties is unpredictable. This is the reason for the next step the work — the study of NaI(Tl, Ca). The most typical photoluminescence features of NaI(Tl,Ca) are shown in Fig. 5. Two overlapped emission bands are revealed in the range of 350–550 nm. The thallium lumi-

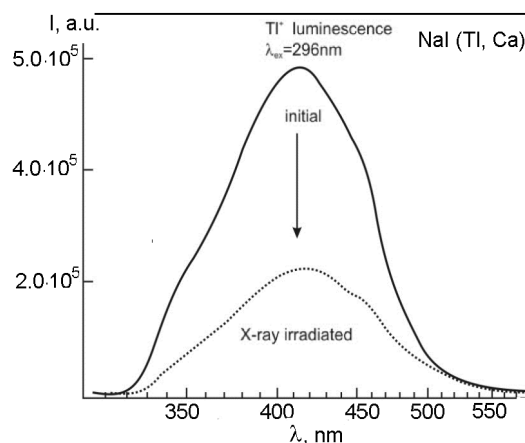


Fig. 6. The quenching of Tl^+ ion emission in NaI(Tl,Ca) crystal (X-ray 110 min irradiation).

nescence band with a maximum at 415 nm is excited in the A-band ($^1S_0 \rightarrow ^3P_1$ transition). Another band at 385 nm becomes excited in more short-wave range and not conditioned by thallium. This band is similar to emission of NaI(Ca) crystal. Significant decrease of both activator and impurity-induced luminescence occurs under irradiation (Fig. 6). We can assume that the quenching could be explained by the appearance of additional absorption in the 360–440 nm range, that is, the effect of reabsorption of luminescence takes place.

It turns out to be rather difficult to judge the change of absorption in the short-wavelength range (<350 nm) due to the overlap with intense transitions $^1S_0 \rightarrow ^3P_{1,2}$; 1P_1 in Tl^+ ions. However, this range is of particular interest, since it characterizes a change in the concentration and composition of the activator and capture centers. To obtain information, a comparison of the optical density difference for the irradiated and initial samples (ΔD) was effective as illustrated by Fig. 7. X-ray irradiation leads to significantly higher colorability, as can be seen in Fig. 8.

A change in the optical density spectrum of a NaI(Tl,Ca) crystal under UV irradiation demonstrates the decrease of absorption typical of Tl^+ ions and the simultaneous appearance of intense 273 and 315 nm peaks on the tail of the activator bands. A similar phenomenon was found in NaI(Tl,Ca,Eu) and NaI(Tl,Sr) crystals. It should be noted that the appearance of such peaks also occurs in NaI(Tl) crystal; however, this is not accompanied by an increase of absorption in the range of 350–500 nm. The results indicate

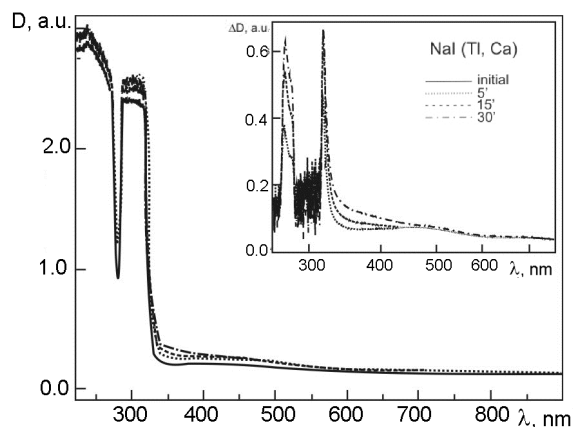


Fig. 7. The UV irradiation effect on the absorption of NaI(Tl,Ca) crystal. Inset: the differences of optical density of initial and irradiated sample.

that, upon irradiation, there is a capture of carriers on thallium. In co-doped crystals, this accompanies by a less efficient process of V-center formation, which determines the reabsorption. Both processes should lead to activator luminescence decrease and hence to a decrease in scintillation yield.

It is important to emphasize that the study of radiation damage in thallium-activated alkali halides and, in particular, NaI(Tl) showed that during irradiation electrons and holes are captured directly by thallium ions [17, 18]. It leads to the creation of Tl^0 and Tl^{2+} centers. The effective $Tl^+ \rightarrow Tl^{2+}$ conversion and the thermal stability of Tl^{2+} ions leads to a decrease in the concentration of active Tl^+ centers and, accordingly, to a decrease in the yield of NaI(Tl). As a result, the crystal partially or completely loses its scintillation efficiency.

3.3. Scintillation properties of crystals

Scintillation parameters of doped and co-doped NaI(Tl) crystals are presented in Table.

Table. Scintillation parameters of Tl doped and co-doped NaI:Tl crystals

Crystal composition	Light output and energy resolution		Induced coloration
	C, %	R, %	
NaI(Tl)	100	5.8–6.2	
NaI(Tl)	92	5.8–7.3	
NaI(Tl,Ca)	67	6.0	yellow
NaI(Tl,Sr)	68	5,6	yellow
NaI(Tl,Ca,Eu)	70–75	5.4	yellow

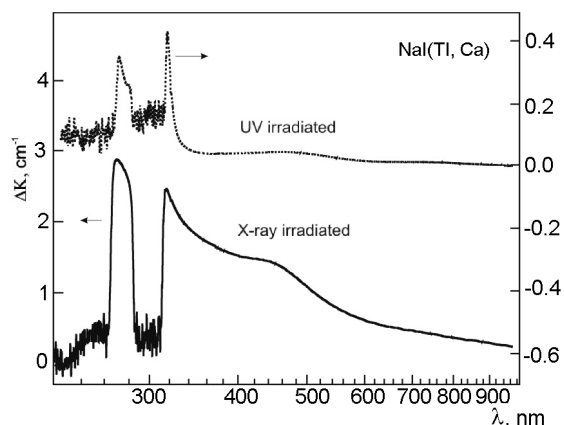


Fig. 8. The impact of UV and X-ray irradiation (5') on the optical absorption of NaI(Tl,Ca) crystal.

Integrating time was 1 μ sec for NaI(Tl), NaI(Tl,Ca) and NaI(Tl,Sr) crystals. The optimal integrating time of 4 μ sec was selected for NaI(Tl,Ca,Eu) due to prolong decay time [5]. The results obtained indicate that the different co-doping slightly improves the energy resolution, but at the same time significantly reduces the light yield. We have to note that similar to shown in [1, 2] the best resolution do not corresponds to the maximal light yield. The spread between these data could be even more significant and the reason of this spread is still not clear.

Studies indicate that co-doping allow to improve energy resolution of NaI(Tl) scintillator but claim for specific approach to technology. Optimal option connects with ability to use divalent ions (Ca, Sr in particular) as scavenger. Calcium binds oxygen due to its high affinity for oxygen [19, 20]. As a result, high-temperature CaO oxide (melting point of 2572°C, density 3.37 g/cm³) is formed (NaI, a melting point of 661°C, ρ 3.67 g/cm³). Typical oxygen luminescence (broad band with maximum ~ 460 nm [3–5]) is suppressed that is typical for efficient scavenger. On the other hand, Ca^{2+} , Sr^{2+} or Eu^{2+} ions partially enter the solid solution and form dipoles of two types: $Ca^{2+}V_c^-$ and $Ca^{2+}O^{2-}$. They are the sources of enhancing yellow color in NaI(Tl,Ca). Moreover, such dipoles are localized near Tl^+ . It leads to formation of activator-containing complex centers. Therefore, it is shown that purification takes place in NaI and CsI, but only in the case of limited contamination of scavenger.

4. Conclusion

In conclusion, it should be noted that there are the potential hidden mechanisms that can deteriorate scintillator performance of NaI(Tl) during irradiation. In fact, it turned out that the formation of hole centers upon irradiation is not the main reason for the decrease in scintillation yield, although its role increases in co-doped crystals. In particular, this is the yellowing effect at high concentrations of codoping ions.

The determining process is the capture of carriers directly by thallium ions with the Tl^+ to Tl^{2+} transformation. As a result, a positive effect of co-doping can be achieved only with a strictly specified balance between these mechanisms. This is reflected, for example, in improvement of energy resolution is achieved only at the optimum concentration of co-dopant, and parameters begin to deteriorate.

References

1. K. Yang, P.R.Menge, *J. Appl. Phys.*, **118**, 213106 (2015).
2. I.V.Khodyuk, S.A.Messina, T.J.Hayden et al., *J. Appl. Phys.*, **118**, 084901 (2015),
3. Inorganic Scintillators for Detector Systems, Physical Principles and Crystal Engineering, ed. by P.Lecoq, A.Gektin, M.Korzhik, Handbook, 2nd Edition, Springer (2017).
4. N.Shiran, I.Boiaryntseva, A.Gektin et al., *Mater. Res. Bulletin*, **59**, 13 (2014).
5. N.V.Shiran, A.V.Gektin, Ya.Boyarintseva et al., *IEEE Trans. Nucl. Sci.*, **57**, 1233 (2010).
6. R.Adhikari, Qi Li, R.T.Williams et al., *J. Appl. Phys.*, **116**, 223703 (2014).
7. Y.Uchida, Y.Nakai, *J. Phys. Soc. Jpn.*, **9**, 928 (1954).
8. R.I.Didyk, M.V.Pashkovski, N.A.Tsal', *Opt. and Spectr.*, **20**, 832 (1966).
9. E.Rzepka, S.Lefrant, L.Taurel, *Rad. Eff. Def. Solids*, **98**, 301 (1986).
10. E.Rzepka, M.Bernard, S.Lefrant, *Nucl. Instrum. Meth. Phys. Res. B*, **32**, 235 (1988).
11. W.J.van Sciver, *Phys. Rev.*, **120**, 1193 (1960).
12. M.P.Fontana, W.J.van Sciver, *Phys. Stat. Sol.*, **37**, 375 (1970).
13. M.Moszynski, W.Czarnacki, A.Syntfeld-Kazuch et al., *IEEE Trans. Nucl. Sci.*, **56**, 1655 (2009).
14. A.V.Andryuschenko, S.Budakovskiy, Yu.Vostretsov et al., *Ukr. Phys. Journ.*, **22**, 1009 (1977).
15. A.Gektin, N.Shiran, S.Vasyukov et.al. *Opt. Mater.*, **35**, 2613 (2013).
16. H.Vrielink, D.G. Zverev, P.Leblans et.al. *Phys. Rev.* **B85**, 144119, (2012).
17. R.G.Kaufman, W.B.Hadley, H.N.Hersh, *IEEE TNS*, **17**, 82 (1970).
18. Qiang Sun, Jinsheng Shi, *J. Lumin.*, **131**, 984 (2011).
19. T.P.Rebrova, V.L.Cherginets, Yu.N.Datsko et al., *Russ. J. Inorg. Chem.*, **57**, 427 (2012).
20. V.L.Cherginets, T.P.Rebrova, Yu.N.Datsko et al., *J. Cryst. Growth*, **380**, 143 (2013).