

Nanodefekt substructures in crystal phosphors

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Abstract. We investigated spectral and kinetic characteristics of the luminescence in alkali halide crystals with polyvalent impurities, crystal phosphors based on metal tungstates in the form of nano-, micro- and bulk crystals. The possibility of the existence of complex defects (nanodefekt) in materials containing high defect concentration is shown.

1. Introduction

The currently existing concepts of the stimulated processes in crystal phosphors with simple structure, with low concentration of the incorporated radiation defects (radiation-induced defects) are considered to be sufficiently consistent. These concepts are used to interpret the processes in complex crystal phosphors with high concentration of initial imperfections (widely used as phosphors, scintillators, and active and dosimetry media). It has been established that the processes in the area under radiation in complex materials with high concentration of imperfections cannot be interpreted within the concepts formulated for simple phosphor crystals. This impedes optimization of the technology for their synthesis and increase in their radiative characteristics under excitation by hard radiation.

A new approach to interpret radiation-induced processes in complex materials with high concentration of imperfections has been proposed in [1-3]. It is assumed that in these crystals, the nanodefekt are formed in the process of synthesis. A nanodefekt is a dopant ion, codopants entered the crystal to compensate for its charge and elastic tension, intrinsic lattice defects (vacancies, interstitial ions of the base), or a complex of defects of the structure in the crystal with low stoichiometry. A luminescence center may be the structural element of the nanodefekt as well.

Nanodefekt can cause significant change in the processes of radiation-induced processes in solids. Electronic excitations in the region of the nanodefekt are expected to decay under laws different from those acting in the lattice. The probability of capturing electronic excitation by nanodefekt, transfer of the excited energy to the luminescence center are supposed to be different from those for perfect crystals with point defects.

Determination of the structure and properties of nanodefekt is a complicated problem. There are no methods for experimental and theoretical studies of complex nano-sized defects. The composition and structure of the nanodefekt depends on the composition and properties of the matrix and material synthesis technology.

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This paper presents the results of the study on the structure of simple scintillation crystals with a high level of imperfection indicating the possible existence of nanodefects in these crystals and their composition.

2. Samples and experimental techniques affiliations

We tested the following crystals:

- LiF-MeO (Me: Li, Fe) grown by Stockbarger method in fluorinating atmosphere in STIMS SC "S.I. Vavilov State Optical Institute" (St. Petersburg).
- LiF-MeO (Me: Ti, W) grown by Kyropoulos method in air in ISMA NAS of Ukraine (Kharkiv).
- macrocrystal ZnWO₄ and ZnWO₄: Eu grown by Czochralski method in air in ISMA NAS of Ukraine (Kharkiv).
- ZnWO₄ and ZnWO₄ nano-sized crystals (nanocrystals): Eu, synthesized in ISMA NAS of Ukraine (Kharkiv) by hydrothermal microwave method. Nanocrystals were two types of particles: grains with a length of ~ 25 nm and rods with a length of 100–200 nm and a diameter of about 5–10 nm. Samples to study the luminescent properties were polymer films of heat-resistant and low-molecular organic silicone rubber with incorporated ZnWO₄:Eu nanocrystals.

The initial imperfection in the tested crystals was estimated from the absorption spectra in the range of 13–0.1 eV. The spectra in the UV range (13–6 eV) were measured in S.I. Vavilov State Optical Institute (St. Petersburg) with a vacuum monochromator-based spectrometer; the spectra in the range of 6–1 eV were measured with SF-256 UVI and SF-256 NIR spectrometers. IR spectra were measured with FT-IR spectrometer Nicolet 5700 in the range of 0.5–0.1 eV with a spectral resolution of 2 cm⁻¹. Spectral and kinetic characteristics of pulsed cathodoluminescence (PCL) and pulsed photoluminescence (PPL) were measured in the spectral range of 4.0–1.6 eV. The characteristics of the exciting electron pulse (EP) were as follows: the length of the pulse was 10 ns; the average electron energy was 250 keV. PCL was excited by radiation of the fourth harmonic of a neodymium laser (photon energy was 4.66 eV) with a pulse duration of 5 ns and the energy per pulse of 40 mJ. The kinetic curves of PCL and PPL at a chosen wavelength were recorded with oscilloscope LeGroy-WP-6030a in the time interval of 1•10⁻⁸–1•10⁻³ s after the end of the excitation pulse.

3. Results and discussion

3.1. The composition of nanodefects in LiF crystals with polyvalent cation-substituent impurities

LiF crystals doped with Fe, Ti, U and W are efficient converters of hard excitation energy into the luminescence. The valence of these ions is different from the valence of Li ions which they replace. Obviously, intrinsic defects, interstitial ions and vacancies enter for compensation of charge and elastic tension in the region of the impurity ion. The crystals with multivalent ions are grown from the mix with metal oxides as added dopants, which means that oxygen ions enter the crystal as well. When oxygen enters LiF crystal, characteristic absorption occurs in the UV spectrum [4-7] in the region from 12.0 (transparency cutoff) to 4.6 eV. If the concentration of oxygen is sufficiently high, the crystal is not transparent in the region above 4.6 eV.

When LiF crystals doped with Fe, Ti and W are exposed to hard radiation pulses: electrons, laser in the region of 4.66 eV, the luminescence is excited in the region of 2.0–3.5 eV. When measured after 10 ns after the end of the excitation pulse, the luminescence spectra in all the crystals have a luminescence band at 3.1 eV (Fig.1). The luminescence at 3.1 eV in LiF crystals is caused by O²⁻ ions not bound with the dopants [8]. Over time after the end of the excitation pulse in the nanosecond range, this band decays. The bands in the long wave-length region become dominant in the spectra. As can be seen in Figure 1, the position of the luminescence bands in the spectra measured after 10 ms depends on the type of the dopant. It is assumed that in LiF-O, LiF-Fe, Ti and W the luminescence center contains O²⁻ ion as a basic structural element [1, 9-11]. It may be assumed that the luminescence center contains a fluorine vacancy. Dependence of the luminescence band on the type of the dopant indicates that the center is in close vicinity to the dopant ion. It can be concluded that the

luminescence in the region of 2.5...3.0 eV in LiF-Me_nO_m crystals is caused by Me-nO²⁻ complexes [12].

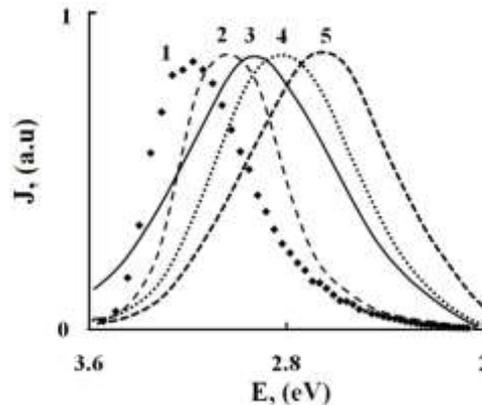


Figure 1. Photoluminescence spectra at 300 K measured with 10 ns (1) and 10 ms (2–5) delay in non-irradiated LiF crystals doped with Li₂O (1, 2), Fe₂O₃ (1, 3), WO₃ (1, 4) and TiO₂ (1, 5).

In IR absorption spectra of LiF doped with W, Ti and Fe, there is a characteristic absorption band in a free state at 3730 cm⁻¹ caused by OH⁻ ions [13,14]. In the spectra of LiF and LiF-Li₂O, the absorption bands caused by OH⁻ ions are not observed. In addition to the band at 3730 cm⁻¹ in IR spectra, in crystals doped with W, Ti and Fe, the bands are found at 3620–3560 cm⁻¹. The position and the number of the bands depend on the type of the dopant cation. The observed dependence of the bands on the type of the dopant cation can be attributed to the effect of the cation on the absorption state of OH⁻ ion. The results indicate that during synthesis of the crystal, OH⁻ ions are located in the vicinity of the dopant ion. We can assume that during of the crystal, Me-n OH⁻ complexes are created in the region of the dopant.

In growing, when polyvalent cations of the impurity enter LiF crystals, anion vacancies enter the crystal and they are located in the area of the impurity ion. The experimental results to prove our conclusion are as follows. Fig. 2 shows the results of the pre-study for the kinetics of the accumulation of F₂ complex color centers. In pure LiF and LiF crystals with oxygen, the accumulation of F₂ centers occurs with an induction period, which is characteristic of their accumulation in alkali halide crystals. In crystals with polyvalent ions, the accumulation is significantly different. The dose dependence of the accumulation of F₂ centers is a curve with saturation. The saturation level of the accumulated F₂ color centers in the dose dependence is defined by the concentration and type of the dopant cation.

The observed differences in the accumulation of F₂ centers in these crystals can be explained as follows. In pure LiF crystals, the formation of F₂ centers is the result of a complex set of processes which are generally defined by the probability of the formation of elementary F centers in spatially close lattice sites. Therefore, the kinetics of F₂ centers accumulation is described by a parabolic function.

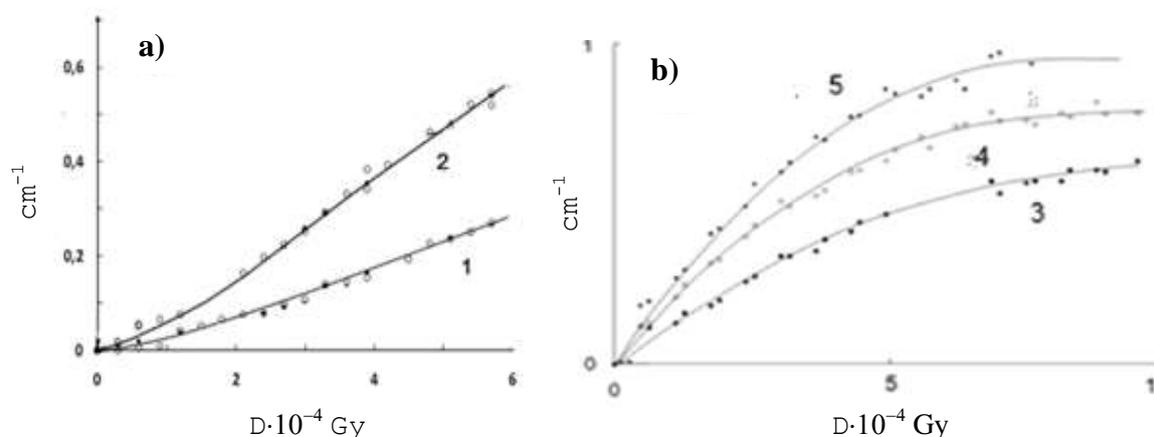


Figure 2. Dose dependence of the absorption coefficient in the maximum of F_2 band under irradiation by electrons at 300 K for different crystals: non-doped LiF (1), LiF-Li₂O (2), LiF-TiO₂ (3), LiF-WO₃ (4) and LiF-Fe₂O₃ (5).

The formation and accumulation of F_2 centers in doped crystals occurs in a different way. Incorporation of the dopant ions (Ti, W and Fe) in LiF crystal is accompanied by the entry of anion vacancies which like other lattice defects (intrinsic and extrinsic) compensate the charge and elastic tension in the region of the incorporated dopant cation. The existence of the anion vacancies in the crystal changes the kinetics of accumulation of complex centers. The accumulation of F_2 centers in doped crystals is expected to occur with a statistical probability proportional to the concentration of the dopant ions. Therefore, the dose dependence of the accumulation of F_2 color centers in crystals doped with heavy ions is a curve with a rapid initial increase in the concentration and saturation as the concentration of free all-in vacancies decreases.

Thus, in LiF crystal doped with ions of polyvalent metal, we can find oxygen ions which entered the crystal with dopants during growing, and $Me-nO^{2-}$ and $Me-n OH^-$ complexes. In the region of the dopant ions, there are ready vacancies (vacancy complexes) that are involved in the formation of F_2 centers. The results obtained show that during synthesis of LiF crystals doped with ions of polyvalent metals, complexes containing oxygen ions, hydroxyl groups and vacancies are formed in the region of the dopant. This type of the complex lattice defects can be regarded as a nano-sized region of the crystal with its spatial and energy structure. This region of the crystal can be called a nanodefekt.

3.2. Possibility of the existence of nanodefects in scintillation crystals based on tungstates

It has been found that spectral characteristics of the radioluminescence of PbMoO₄ and CaMoO₄, CaWO₄, PbWO₄, CdWO₄; CdWO₄-Li₂CO₃; CdWO₄-Li₂CO₃-Bi₂O₃, LiF:WO₃, Li₂W_{0.95}Mo_{0.05}O₄ and suchlike crystals are similar. In the luminescence spectra of the crystals we observe the band with a maximum at 2.4–2.7 eV with a half-width at ~ 0.6 – 0.7 eV, and the decay time at room temperature of several tens of microseconds [12,15–20]. Close values of the spectral and kinetic parameters of the excited luminescence in oxygen-containing materials, different both by the type of the crystal lattice, and by the type of co-dopants, suggest that the structure of radiative centers have something in common.

Crystals of tungstates and molybdates are grown typically by Czochralski method from the molten mixture made by mixing the oxides of Zn, Pb and Cd and oxides of tungsten, molybdenum in proportions required to make a stoichiometric composition. It is obvious that during this growing the crystal contains a great amount of lattice defects that must have an effect on the characteristics of the material. In [12], it is suggested that in crystals with high level of imperfection, which are tungstates, molybdates, as well as in LiF crystals doped with polyvalent ions, we can find complex defects (nanodefects) as a set of intrinsic lattice defects, impurity ions entered during growth, among which

we can find OH^- ions. The luminescence centers in metal tungstate crystals, as well as in the doped LiF crystals, are oxygen-containing complexes.

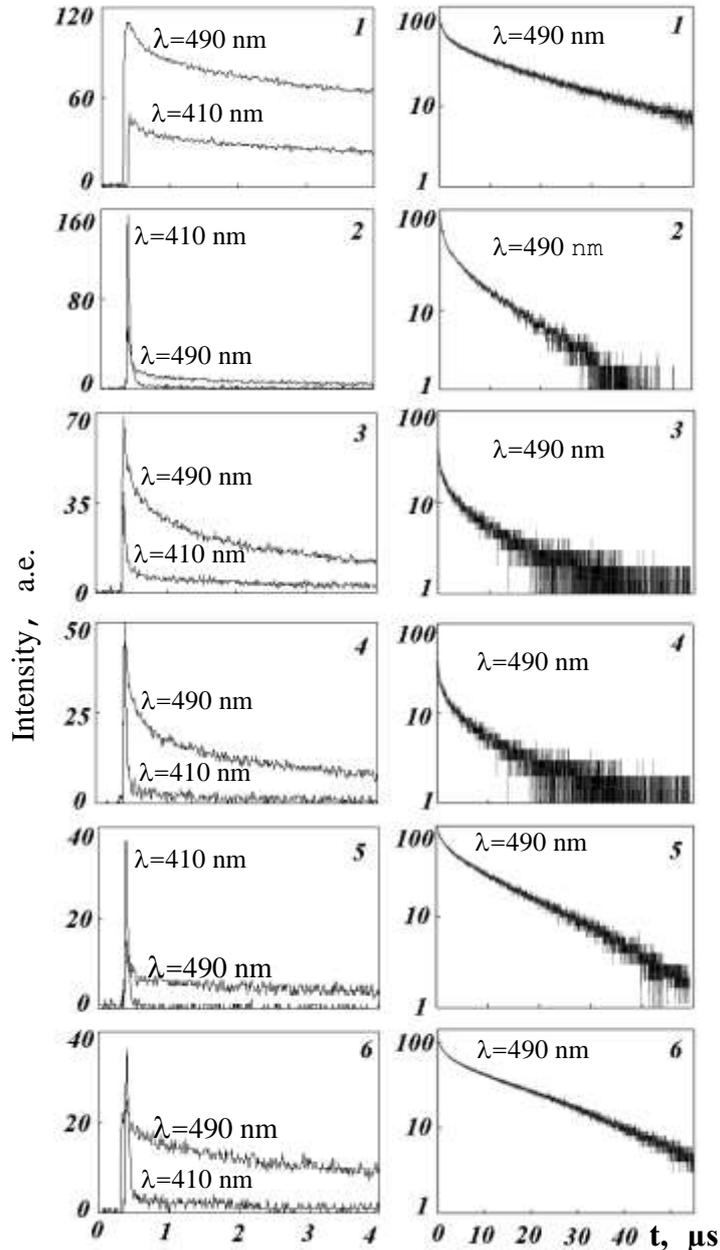


Figure 3. Kinetic curves of PCL decay for ZnWO_4 crystals of different dispersion incorporated into the polymer matrix. 1 is ZnWO_4 macrocrystal; 2 is with nanocrystals in the form of grains with a size of 25 nm, 3 is with nanocrystals in the form of rods with a length of 50–100 nm and a diameter of 5–7 nm; 4 is with nanocrystals in the form of rods with a length of 150–200 nm and a diameter of 10 nm; 5 is with crushed crystals, the size of the dominant particles being 250 nm; 6 is with crushed crystals with the size of the dominant particles being $\leq 250 \mu\text{m}$.

We have studied the kinetic curves of attenuation of pulsed cathodoluminescence in ZnWO_4 crystals of different dispersion incorporated into the polymer matrix, and single crystals. The luminescence decay kinetics at 490 nm (2.53 eV) has two distinct stages of decay: in the range of 1–2 μs and 5–30 μs in different crystals. There is a significant difference in the kinetic curves of the luminescence decay in samples with synthesized nanocrystals and samples with crushed single crystals in a microsecond range. The characteristic decay time of the luminescence in samples 1, 5 and 6 (single crystal and crushed crystals) are 26, 13 and 15 μs , respectively. The characteristic times of the kinetics of the luminescence decay in crystals with synthesized nanocrystals with the size that does not exceed 200 nm are 5, 7 and 7 μs (samples 2, 3 and 4, respectively). The distinction in the characteristics of the luminescence decay kinetics may be due to the relationship between the size of the nanod defect, which contains the luminescence center, and the crystal. A sharp change in the characteristic times of the luminescence decay as the crystal size reduces to the units of nanometers can be attributed to the fact that the sizes of the crystals and nanod defects become commensurable. Note that short time luminescence can be observed in the region at 410 nm (3.03 eV) which decays after 100 ns, and it is more distinct in fine-dispersed crystals. Apparently, other centers possibly related to the surface are responsible for the luminescence in this area [12].

Fig. 4 shows the results obtained for the kinetics of the luminescence in ZnWO_4 macro- and nanocrystals doped with europium. The kinetic curves indicate the luminescence decay in the band at 2.6 eV (480 nm), which is caused by the oxygen complex luminescence centers in the nanod defect, and in the band at 614 nm caused by europium. The spectral and kinetic characteristics of emission from europium are weakly dependent on the size of the crystal: the spectra in macro- and nanocrystals are identical. The characteristic decay time of the luminescence at 614 nm differs slightly: in the macrocrystal it is 0.5 ms, and in the nanocrystal it is 0.3 ms.

The spectral characteristics of the luminescence in the band at ~ 480 nm, which is caused by the centers with an oxygen ion being the structural element, are identical in all the tested crystals, and this indicates the identical nature of the luminescence centers responsible for this band. However, the kinetic characteristics of the luminescence in macrocrystals and nano-sized crystals are significantly different; they are 15 μs and 3 μs , respectively. The possible cause of the difference can be as follows. The oxygen center responsible for the luminescence is a component of the nanod defect. The size of the nanod defect is several nanometers, which is comparable to the size of the nanocrystal. The size of the europium ion even coupled with the donor is less than a nanometer. Therefore, the effect of the crystal surface with the sizes of 10 ... 25 nm on the radiative properties of the oxygen luminescence center in the nanod defect is much larger than relaxation of the excitation in the europium center.

The presented results support the hypothesis that in zinc tungstate crystals having a high level of initial defects due to non-stoichiometry, complex defects with sizes of several nanometers are formed. A nanod defects in this crystal is the region of the crystal with different spatial and energy structure.

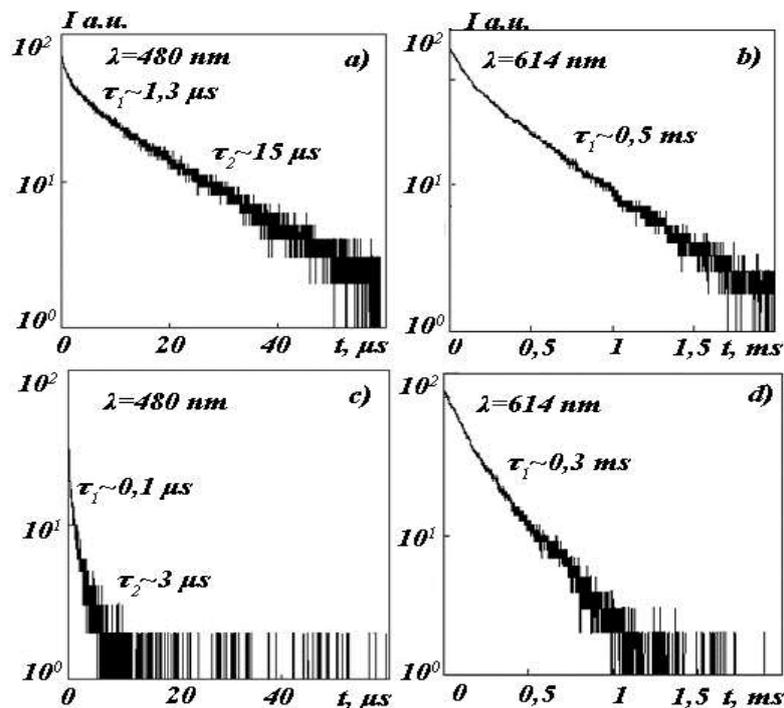


Figure 4. Decay kinetics of ICL in the bands at 480 and 614 nm for macrocrystals (a,b) and nanocrystals (c,d) doped with 3 mol% Eu under excitation by electron beam.

4. Conclusion

The nanodefekt substructure in crystal phosphors can lead to sufficient increase in the efficiency of the luminescence under excitation. Nanodefekts must have a very large capture cross section of the carriers of charge, energy. With a radius of nanodefekts equal to 3...4 interatomic distances, the capture cross section of the hole in the region of the nanodefekt 200 ... 500 times exceeds that of the random site in the crystal.

In the case of the recombination character of the energy transfer to the luminescence center, the probability of recombination in the region of the nanodefekt can be much higher than that in the crystal. The luminescence through the recombination mechanism of excitation in the nanodefekt can be as follows. Radiation-induced electrons and holes are found in the area influenced by nanodefekts due to their large capture cross sections. A hot mobile hole, when it appears in the relaxed region of the nanodefekt, is immediately self-trapped, it captures an electron. The energy of the near-impurity self-trapped exciton is transmitted to the luminescence center. If the lifetime of the near-impurity exciton is much greater than the lifetime of the luminescence center in an excited state, the probability of the energy transfer to the luminescence center is supposed to be close to unity. This ratio is always fulfilled for scintillators: the lifetime of the near-impurity self-trapped exciton is of the order of 10^{-4} ... 10^{-6} . The lifetime of the near-impurity excitons in KCl-J crystal is about 10^{-5} s [21–23].

The approach based on the existence of the nanodefekt substructure opens up new possibilities for the analysis of radiation-induced processes in crystals with a high level of imperfection which are used as functional materials.

Acknowledgments

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- [1] Lisitsyna L A, Oleshko V I, Putintseva S N and Lisitsyn V M 2008 *Optics and Spectroscopy*. **105**,**40** 531
- [2] Lisitsyna L A, Korepanov V I at al. 2012 *Optics and Spectroscopy*. **112** **6** 175
- [3] Lisitsyna L A, Lisitsyn V M 2013 *Japan. J. Appl. Phys.* **55** **11** 2297
- [4] Lisitsyna L A, Putintseva S N, Lisitsyn V M, Oleshko V I 2008 *Nonorganic materials*. **6** 754
- [5] Freytag E 1964 *Z. Phys.* **177** 206
- [6] Shvarts K K, Kristapson Ya Zh, Lusia D Yu, Podlin A V *Proc.: Radiation Physics.V*, ed. K K Shvarts, Lushina A F. Zinatne. Riga, 1967 179.
- [7] Korzhik M V. 2003 *Physics of scintillators based oxygen single crystals* (Minsk: Belarusian State University)
- [8] Lammers M J J, Blasse G, Robertson D S 1981 *Phys. Stat. Sol. (a)* **63** 569
- [9] Egranov A V, Radjabov E A 1992 *Spectroscopy of oxygen and hydrogen impurity centers in alkali halide crystals* (Novosibirsk: Nauka)
- [10] Jain V K 1986 *J. Phys. D: Appl. Phys.* **19** **9** 1791
- [11] Rebane L A 1968 *Proc. IAA AS ESSR*. **37** 14
- [12] Lisitsyna L A, Korepanov V I, Lisitsyn V M at al. 2011 *Optics and Spectroscopy*. **4** **110** 568
- [13] Stoebe G 1970 *J. Phys. Chem. Solids*. **31** 1291
- [14] Wedding B, Klein M 1969 *Phys. Rev.* **177** 1274
- [15] Kolobanov V N, Kamenskikh I A, Mikhailin V V at al. 2002 *Nuclear Instruments and Methods in Physics Research A* **486** 496
- [16] Nagirnyia V, Kirm M, Kotlov A at al. 2003 *Journal of Luminescence* **102-103** 597
- [17] Barinova O P, Kirsanova S V, Kolobanov V N, Mikhailin V V, Spassky D A 2008 *Perspective materials* **4** 34
- [18] Spassky D, Ivanov S, Kitaeva I at al. 2005 *Phys. Stat. Sol.* **2** 65
- [19] Groenink J A, Blasse G 1980 *J. of solid state chem.* **32** 9
- [20] Mikhaik V B, Kraus H, Itoh M, Iri D, Uchida M 2005 *J.Phys.: Condens. Matter*. **17** 7209
- [21] Lisitsyn V M, Malyshev A A, Yakovlev V Yu 1983 *Russian Phys. J.*. **25** **11** 3356
- [22] Lisitsyn V M, Korepanov V I, Strezh V V, Bochkanov P V, Malushev A A 1985 *Russian Phys. J.* **27** **10** 3052
- [23] Korepanov V I, Lisitsyn V M, Lisitsyna L A 1997 *Russian Phys. J.* **39** **11** 1082