Electron-Phonon Interaction of Color Centers in MgF$_2$ and LiF-O,OH Crystals

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Abstract. Low-temperature absorption spectra at temperatures of range of 7.2–300 K in MgF$_2$ and LiF-O,OH crystals were studied to investigate the electron-phonon interaction of radiation-induced color centers in these crystals. The coupling strength (*S*) with the phonons of the lattice of electronic-vibrational transitions was determined from the ratio of intensities in the zero-phonon line and the integrated absorption band. The nature of the color centers associated eith the absorption band at 390 nm and the emission at 490 nm in LiF-O,OH crystals and for the absorption band at 370 nm and the emission at 420 nm in MgF$_2$ crystals was determined from value of *S*.

INTRODUCTION

Laser recording of digital and visual information in three-dimensional and multilayer optical systems is one of the sections of photonics [1,2]. Martynovich et al. [3] developed a new method for laser recording of three-dimensional color luminescent images in the volume of an optical medium based on lithium fluoride crystals with F$_2$ and F$_3^+$ color centers. However, method utilizing these centers does not allow recording a full-color image in accordance with the additive RGB model. This model describes the method of color coding using the three primary colors (red, green and blue), and the luminescence of these two types of centers is observed only in the green and red regions of the spectrum: F$_3^+$ centers with $\lambda_m = 545$ nm, green luminescence, F$_2$ centers with $\lambda_m = 670$ nm, red luminescence. The formation of color centers in LiF that emit in the blue range was first reported by Okuda [4]. At the same time, the structure and model of the detected centers have not been reliably established and require further study.

In our opinion, another object promising for recording full-color images is MgF$_2$ crystal with color centers exhibiting emission bands at 420 nm ($\lambda_{exc} = 375$ nm); 552 nm ($\lambda_{exc} = 266$ nm); 585–620 nm ($\lambda_{exc} = 405$ nm) [5]. The model of these centers has also not been reliably established, despite a number of published works [6–9] devoted to their study.

Taking into account the presence of zero-phonon lines (ZPL) in the low-temperature absorption spectra of these color centers in LiF and MgF$_2$ crystals, we are able to evaluate the electron-phonon coupling and to determine the type of centers by its value. Thus, the coupling strength (*S*) of the electronic transition with the phonons of the lattice is an important parameter defining the type of color center. To estimate *S*, it is necessary to plot temperature dependency graph in the coordinates

$$ln(I_0/I) = f(1 + 2\pi^2 T^2/3T_D^2),\qquad(1)$$

where T is the measurement temperature, T_D is the Debye temperature, which was estimated with the number of particles in the unit cell accounted. The slope of the straight line plotted in the aforementioned coordinates will be equal to the value of the electron-phonon coupling strength. This follows from the exponential decrease in the intensity of the zero-phonon line (I_0):

$$I_0/I = exp[-S(1 + 2\pi^2 T^2/3T_D^2)], \qquad (2)$$

where I is the intensity in the integrated absorption band [10].

EXPERIMENTAL PART

Single crystals of lithium fluoride were grown from industrial raw materials by the Kyropoulos method in air and doped with oxygen. To do this, the samples were either activated by lithium nitrite (this salt is thermally unstable and, when heated to the melting point of LiF decomposes to form Li_2O) during the growth process, or the melt was kept in air for a long time. The crystals were irradiated with γ-radiation at temperature of about 273 K in order to get a high concentration of F_3^+ centers. Optical bleaching was carried out by integrated light of INP 3-7/120 xenon pulse lamps in a KVANT-17 laser illuminator with energy about 50 J per pulse.

Magnesium fluoride single crystals were also grown from industrial raw materials. Irradiation of the crystals was carried out with use of pulsed linear accelerator (ILU-12) with electron energy about of 5 MeV.

Absorption spectra were measured on a Perkin-Elmer-Lambda 950 spectrophotometer (0.1 nm gap) in a closed-loop helium cryostat at temperatures of range of 7.2–300 K.

EXPERIMENTAL RESULTS AND DISCUSSION

LiF-O,OH Crystal

At present time, two models of centers with an absorption band of 390 nm and an emission band of 490 nm have been proposed: the F_3 model in oxygen-free crystals [4,11] and the F_3^+ like model $(F_3^+)^*$ in LiF-O,OH crystals [12,13]. The first mention of these centers is found in the Okuda's work [4]: absorption band at 380 nm with a width of 27 nm, and radiation band at 490 nm with a width 84 nm were observed in experiments with oxygen-free crystals. The structure of the color center (F_3 with the center of symmetry C_{2v}) was proposed after studying the luminescence polarization of these defects. In a later work, Voitovich et al. [11] shared the same point of view on the nature and structure of the centers under study. They also noted that UV treatment increases the concentration of these defects. This experimental fact must be taken into account when considering the mechanism of formation of the studied defects.

Since low-temperature irradiation is used in the technology of formation of centers at 390 nm, which also leads to an increase in the efficiency of formation of F_2^+ like centers, a number of authors have proposed a model of F_3^+ like centers. Ivanov [12] noted similarity of the properties of F_3^+ and centers exhibiting absorption band of 390 nm. This similarity consists in the presence of metastable states in both centers. The simultaneous appearance of ZPL of F_3^+ centers and centers at 390 nm during annealing of LiF-OH crystals, as well as coincidence of the kinetics of center accumulation during irradiation, allowed to attribute the band at 390 nm to $(F_3^+)^*$ centers, which is an F_3^+ center perturbed by radiolysis products OH. Basiev et al. [13] also proposed a model of $(F_3^+)^*$ defects for these centers based on the coincidence of the lifetime of radiative transitions. The electron lifetime in the excited state of the centers under study is 7.2 ns, which is very close that of F_3^+ centers ($\tau = 11$ ns). As one can see from the analysis of literature data, consensus regarding the nature of the blue luminescence has not been reached. The aim of this work is to determine the nature of the centers responsible for luminescence in this spectral region.

The normalized emission spectra of LiF-O,OH samples γ-irradiated (curve 1) and subjected to optical bleaching with UV radiation (curve 2), excited by light emitting diode (LED) with $\lambda_m = 397$ nm are shown in Fig. 1. As we noted above, UV radiation treatment creates the maximum concentration of the studied color centers.
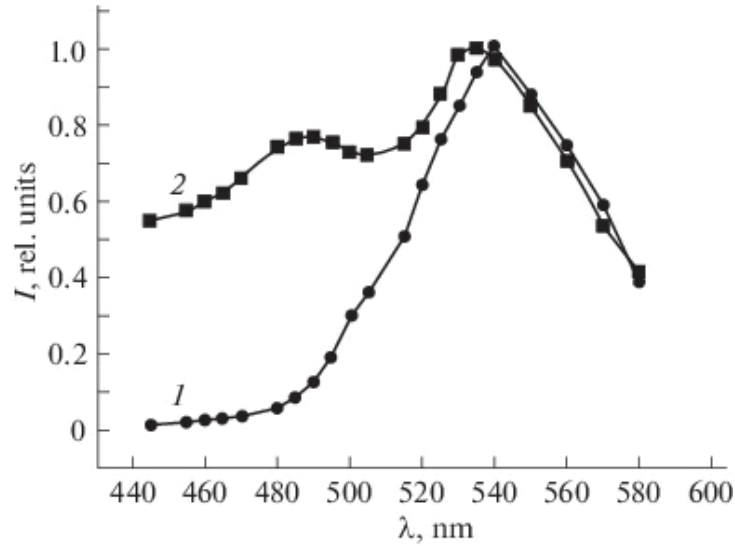
FIGURE 1. Normalized emission spectra of LiF-O,OH sample γ-irradiated (1) with dose of $7.7 \cdot 10^3$ C/kg (300 K) + $1 \cdot 10^4$ C/kg (273 K) and optically bleached (2)

In the absorption spectrum (Fig. 2), bands with $\lambda = 390$ nm (the centers under study), 450 nm (F_3^+), and bands in the range 500–550 nm are observed, the nature of latter has been established and discussed in [14].

(a)   (b)
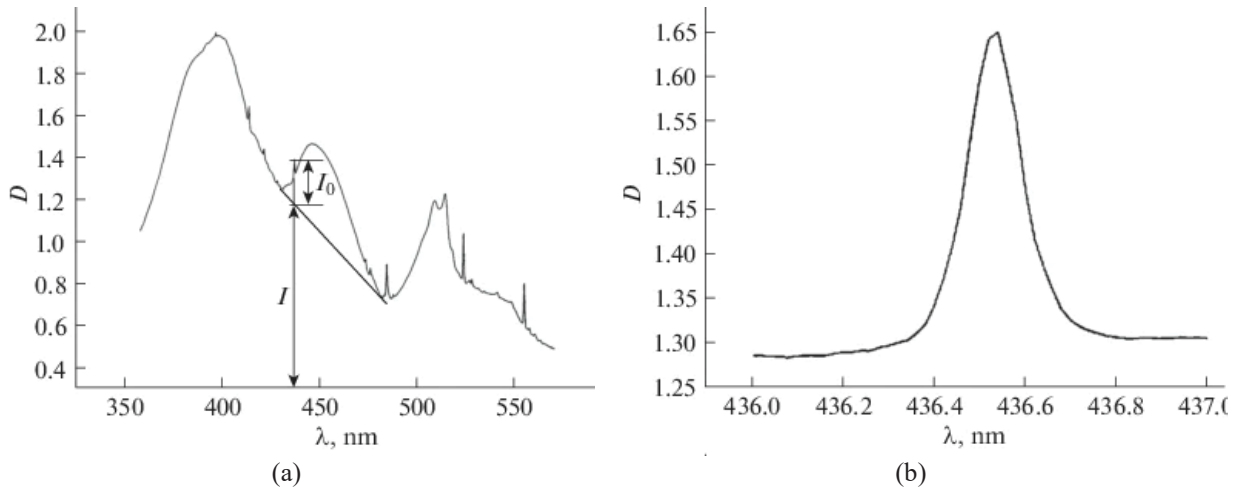
FIGURE 2. Absorption spectrum of sample of LiF-O,OH irradiated with dose of $7.7 \cdot 10^3$ C/kg (300 K) + $1 \cdot 10^4$ C/kg (273 K) and optically bleached, measured at $T = 7.3$ K (a). Fragment of the spectrum corresponding to the zero-phonon line 436.5 nm (b)

Latter defects play a significant role in the formation of the studied color centers and will be discussed below. The 390 nm band exhibits a zero-phonon line at 436.5 nm and a number of weak peaks at 391.06; 395.83; 406.3; 421.05 nm, possibly associated with other color centers. The absorption (390 nm) and emission (490 nm) bands are located symmetrically with respect to the position of the ZPL at 436.5 nm. The temperature dependency graph was plotted for this line (Fig. 3, 1).

The presence of ZPL of the centers under study makes it possible to estimate the strength of the electron-phonon coupling and determine the type of center by this estimate. Two straight lines can be distinguished in the temperature dependence of $\ln(I_0/I)$ (Fig. 3): in the low-temperature region with parameter $S_1 = 4.3$ and in the high-temperature region with $S_2 = 27$. The obtained values of the coupling strength indicate that defects with strong coupling ($S_2 = 27$) with phonons of the lattice appear in the high-temperature region, and weak bonds with weak coupling ($S_1 = 4.3$) – in the low-temperature region.
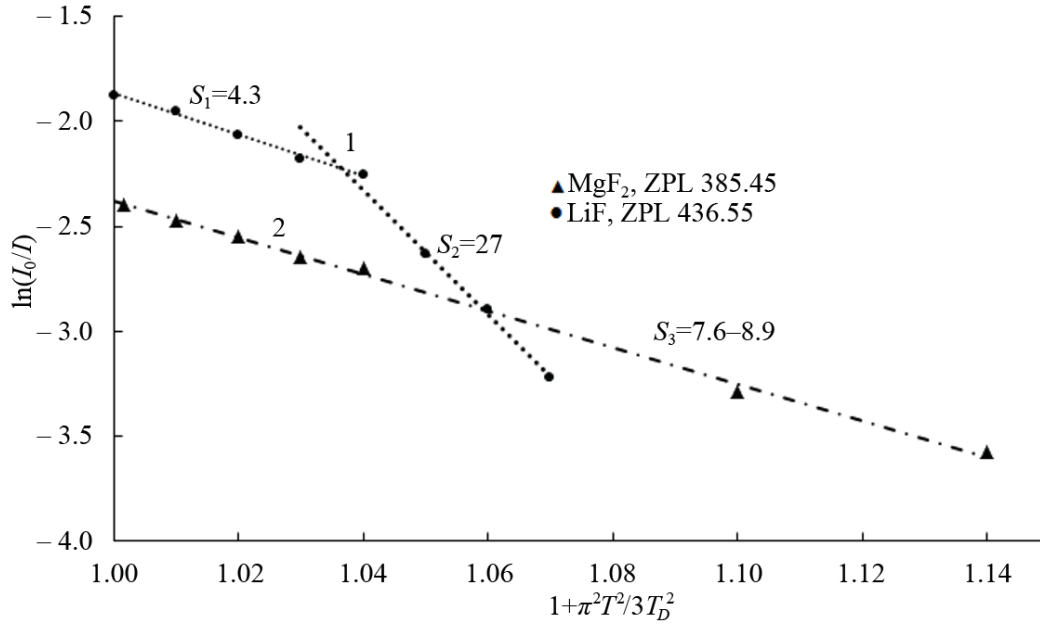
FIGURE 3. Dependency graph $\ln(I_0/I) = f(1+2\pi^2T^2/3T_D^2)$ for ZPL 436.55 nm in the LiF-O,OH crystal (1) and PL 385.45 nm in the MgF$_2$ crystal (2)

Comparing the obtained values with the coupling strength of the electronic transition with the phonons of the lattice for different color centers in LiF crystals, given in Table 1 [10,15,16], we can attribute the weak-binding centers ($S_1 = 4.3$) to F$_3$ centers.

As one can see from the table, the index S for F$_3$ centers is 3.9, while the value we obtained is $S_1 = 4.3$. The observed difference is within the measurement error (10%). However, the concentration of F$_3$ centers in oxygen crystals is insignificant and charged F$_3^+$-centers prevail.

TABLE 1. The coupling strength of the electronic transition with the phonons of the lattice for various color centers in MgF$_2$ [9], LiF [10,15,16] crystals.

Color center type	Crystal	I_0/I (0 K)	S
N$_1$(F$_4$)	LiF	~ 0.37	1
R$_2$(F$_3$)	LiF	0.02	3.9
F$_2^-$	LiF	0.03	3.5
F$_3^+$	LiF	0.005	9.76
M(F$_2$)	LiF	$3\cdot10^{-4}$	8
F	LiF	$\sim 10^{-17}$	40
F	MgF$_2$	-	46
F$_2$	MgF$_2$	-	5

Considering the presence of a metastable state in the studied color centers, we come to the conclusion that other defects are responsible for the blue luminescence. Metastable states are observed at two-electron centers as a result of population of triplet levels with a total spin quantum number $s = 1$. In addition, F$_3$ centers should also be observed in the initial γ-irradiated crystals, however, the blue luminescence is effectively induced as a result of optical bleaching by integrated light of xenon lamps (Fig. 1, curve 2). When the crystal is exposed to UV radiation the interaction of defects with an interstitial halogen in the reaction F$_n$ + H(i$_a^0$) $\rightarrow$ F$_{n-1}$ occurs, as a result of this the crystal is discolored. Along with this reaction, the following transformations take place [14]: (F$_3^+$)* + Li$^+$ $\rightarrow$ FV$_a^+$V$_a^+$ + Li^0 $\rightarrow$ F$_L$V$_a^+$ + V$_a^+$V$_c^-$. As a result of this action, the electron density of F$_3^+$ center (in excited state), shifts to the nearest lithium cation that becomes lithium atom which shifts to the [111] plane. Such defect, Li^0 located in the plane of the F-center is denoted as F$_L$ = Li^0 + F. F$_3^+$ centers convert to F$_L$V$_a^+$ centers

exhibiting an absorption band in the region at 510 nm. Positively charged, they capture an electron and transform into two-electron point defects with an absorption band at 390 nm (F_LF) [14].

The electron-phonon interaction with the index $S_2 = 27$, with strong coupling to the phonons of the lattice, also corresponds to this model. Considering that $S = 40$ for F centers, the presence of lithium atom in the plane of the F center weakens electron-phonon interaction of the electronic transition of the complex two-electron center (F_LF).

The presence of metastable state, the effective formation of the studied defects in optically bleached crystals, the detection of strong electron-phonon coupling ($S_2 = 27$) allows us to state that F_LF defects are responsible for the blue luminescence.

MgF₂ Crystal

At present time two models of centers in MgF₂ crystal with an absorption band at 370 nm and emission at 420 nm are known: F₂ [6,7] and F' centers [8]. Facey et al. [9] demonstrated that there is a dichroism in the absorption of band at 370 nm with electric vector perpendicular to the optical axis of the crystal and there is a zero-phonon line at 387.2 nm, its temperature dependence can be used to estimate parameter S.

The bands with $\lambda_m = 260$ nm (F-center) and $\lambda_m = 370$ nm (the centers under study) are observed in absorption spectrum (Fig. 4 (a)). The 370 nm band has zero-phonon line and phonon replicas, which appear in spectrum even at $T = 90$ K: 380.2; 382.3; 384.2; 385.45 and 387.04 nm.
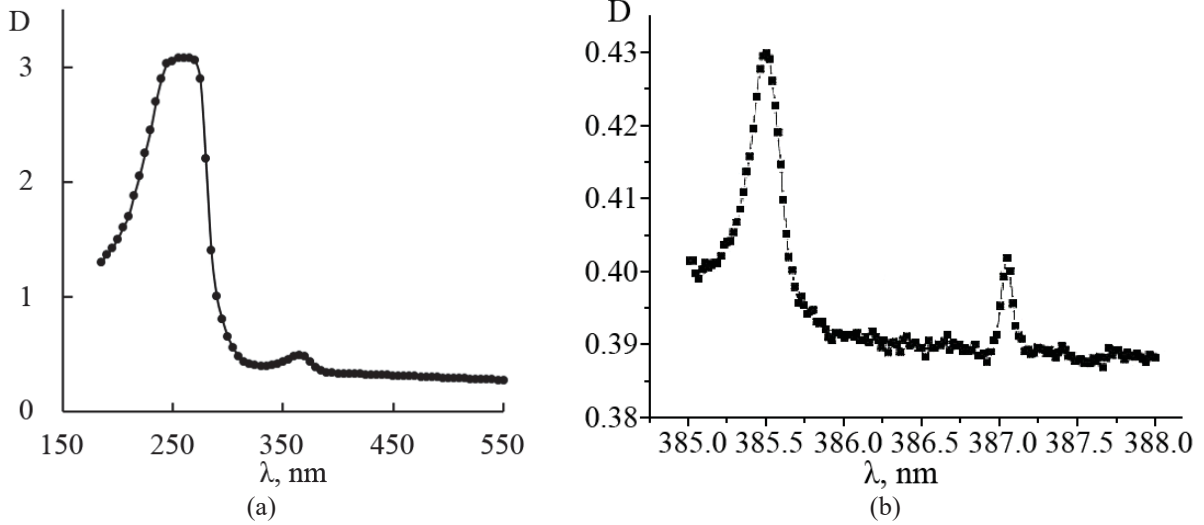
FIGURE 4. Absorption spectrum of an MgF₂ crystal irradiated with electrons, measurement temperature 300 K (a). Fragment of the absorption spectrum of the MgF₂ crystal with ZPL at 387.04 nm, measurement temperature 7 K (b)

The fragment of the absorption spectrum with the most intense phonon replica at 385.45 nm is shown in Fig. 4 (b). The temperature dependency graph was plotted for this line (Fig. 3, line 2). The slope of the straight line plotted in aforementioned coordinates is 8.9. It should be noted that the value of Debye temperature is 490 K, estimated by Kashnow et al. [17] from the maximum phonon frequency at the edge of the first Brillouin zone. For this value, we got $S = 7.6$. Let us compare the obtained values with the coupling strength of electronic transition with phonons of lattice for various color centers in MgF₂ and LiF crystals shown in Table 1. After analyzing this data, we can state that the 387.04 nm ZPL is related to F₂ centers. If the transitions were observed at the F'-center, the coupling strength would be approaching to ~ 20. This follows from comparison of the S values for F₂ (5–8), F₂⁻ (3.5) and F centers (40–46) in LiF and MgF₂ crystals (see Table 1). It should be noted that if $S = 5$ for F₂ centers in MgF₂ crystals, then the phonon energy, estimated with accounting the Stokes shift according to the formula: $E_{abs} - E_{rad} = 2Sh\nu_{ph}$, has value of 325.78 cm⁻¹. The experimentally observed value of $h\nu_{ph} = 106.85$ cm⁻¹ [9]. As one can see, the estimated value of the phonon energy is 3 times higher than the experimentally observed one. We obtained the value $S = 7.6–8.9$, determining the coupling strength of electrons with the phonons of the lattice, from the ratio of intensities in the photoluminescence and the integrated absorption band. The calculated phonon energy in this case is 183.026 cm⁻¹. As one can see, this value is closer to the result of the experiment. Most researchers do not deny the

existence of F' centers. Thus, Vilchinskaya et al. [18] note that F' centers are unstable and are destroyed at room temperature with a time constant about of 300 ns in crystals irradiated with ionizing radiation. Diffusion processes occur in MgF_2 crystals irradiated with electrons under influence of the fourth harmonic of a neodymium laser radiation (266 nm) at local temperature established in laser beam channel (f_{rep} = 12.5 Hz, τ = 10 ns, average power 10 mW, 10^4 pulses) [19]. We can assume that the Crawford mechanism of the formation of F_2 centers is observed: $F \rightarrow V_a^+ + e$; $F + e \rightarrow F'$; $F' + V_a^+ \rightarrow F_2$. In this case, the average time of motion of the anionic vacancy is about 40 minutes.

CONCLUSION

The coupling strength of the electronic transition with phonons of the lattice in LiF-O,OH crystals corresponding to the absorption band of 390 nm (S = 4.3 and 27.0) and in MgF_2 crystals for the absorption band of 370 nm (S = 7.6–8.9) was determined. Assumption about the nature of the unknown color center responsible for the observed electronic transition was made, based on the parameter S. Based on the value of S, priority is given to two-electron F_LF centers with strong bond in LiF-O,OH crystals, and to F_2 centers in MgF_2 crystals. F_2 centers are optically stable and promising both as working centers of active laser elements and for laser recording of digital and visual information in three-dimensional and multilayer optical media.

ACKNOWLEDGMENTS

REFERENCES

1. N. Marquestaut, Y. Petit, A. Royon, P. Mounaix, T. Cardinal, and L. Canioni, Adv. Funct. Mater **24** (37), 5824–5832 (2014).
2. T. Pikuz, A. Faenov, T. Matsuoka, S. Matsuyama, K. Yamauchi, N. Ozaki, B. Albertazzi, Y. Inubushi, M. Yabashi, K. Tono, Y. Satom H. Yumoto, H. Ohashi, S. Pikuz, A. N. Grum-Grzhimailo, M. Nishikino, T. Kawachi, T. Ishikawa, R. Kodama, Sci. Rep. **5**, 17713 (2015).
3. E. F. Martynovich, E. O. Chernova, V. P. Dresvyansky, R.F. Patent No. 2653575 (2018).
4. A. Okuda, J. Phys. Soc. Jpn. **16**, 1746–1762 (1961).
5. L. I. Bryukvina, E. F. Martynovich, Izv. Vyssh. Uchebn. Zaved., Fiz. **56** (2-2), 73–76 (2013).
6. T. Fujita, K. Takiyama, M. Nishi, Mem. Fac. Eng., Hiroshima Univ. **3**, 21–27 (1978).
7. A. P. Sergeev, P. B. Sergeev, V. D. Zvorykin, Izv. Vyssh. Uchebn. Zaved., Fiz. **49** (S10), 312–315 (2006). Available at http://conferences-2008.hcei.tsc.ru/cat/proc_2006/rpc/Paper_088.pdf.
8. V. I. Baryshnikov, T. A. Kolesnikova, L. I. Shchepina, S. V. Dorokhov, G. V. Sotserdotova, Opt. Spektrosk. **67**, 217–221 (1989).
9. O. E. Facey, W. A. Sibley, Phys. Rev. **186**, 926–932 (1969).
10. D. B. Fitchen, "Zero-Phonon Transitions," in *Physics of Color Centers*, edited by W. B. Fowler (Academic Press, New York, London, 1968), p. 293–350.
11. A. P. Voitovich, V. S. Kalinov, E. F. Martynovich, A. P. Stupak, L. P. Runets, Cryst. Res. Technol. **48**, 381–386 (2013).
12. N. A. Ivanov, "F-agregatnye tsentry okraski v kristallakh LiF i NaF i optimizatsiya parametrov opticheskikh lazernykh elementov na ikh osnove," Cand. Sc. (Phys.-Math.) thesis, Irkutsk State University, Irkutsk, 1985.
13. T. T. Basiev, I. V. Ermakov, K. K. Pukhov, Fiz. Tv. Tela **39**, 1373–1379 (1997) [Phys. Solid State **39**, 1218–1223 (1997)].
14. L. I. Shchepina, S. S. Kolesnikov, V. M. Kalikhman, I. V. Teryaeva, Opt. Spektrosk. **90**, 622–624 (2001) [Opt. Spectrosc. **90**, 552–554 (2001)].
15. N. D. Vieira Jr., I. M. Ranieri, S. P. Morato, Phys. Status Solidi A **73**, K115–K120 (1982).
16. R. Gadonas, R. Danelyus, V. Kamalov, Izv. Akad. Nauk SSSR, Ser. Fiz. **46**, 1979–1984 (1982).
17. R. A. Kashnow, K. A. McCarthy, J. Phys. Chem. Solids **30**, 813–818 (1969).

18. S. S. Vilchinskaya, V. I. Korepanov, Izv. Vyssh. Uchebn. Zaved., Fiz. **49** (S10), 94–98 (2006). Available at http://conferences-2008.hcei.tsc.ru/cat/proc_2006/rpc/Paper_025.pdf.
19. L. I. Shchepina, Izv. Vyssh. Uchebn. Zaved., Fiz. **52** (8-2), 200–204 (2009).