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CONDENSED-MATTER SPECTROSCOPY

Efficiency of Formation of Quasi-Metallic Defects in Alkali–Halide Crystals

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Abstract—The formation of quasi-metallic defects on the basis of the F_L center (F center with a metal atom) has been investigated with the aim of increasing the efficiency and decreasing the pump threshold of laser elements based on alkali–halide crystals. The regularity of formation of quasi-metallic defects in a number of alkali–halide crystals has been established.

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F_2 and F_3^+ color centers have a high quantum efficiency (close to unity for LiF crystals); hence, they are of interest in view of the fabrication of miniature optical devices on their basis [1] and distributed-feedback lasers in the visible spectral range [2]. In fluorine lithium crystals, as a result of radiative and photothermal effects, quasi-metallic centers are formed on the basis of F_L defects (lithium atoms in F centers) [3]. A mechanism of formation of quasi-metallic defects is proposed. It is shown that, due to the classical configuration of F_3 and F_3^+ centers, favorable conditions arise for the localization of an electron at the nearest regular alkaline metal cation with the simultaneous capture of the formed atom by one of three (in the case of an F_3 center) or two (in the case of an F_3^+ center) F centers under optical, thermal, and radiative actions [4, 5]. These defects cause losses in the spectral pump and emission regions of active elements, thus deteriorating the parameters of laser elements (efficiency and pump threshold). The purpose of this study is to establish the regularity of the formation of quasi-metallic defects in a number of alkali halide crystals (AHCs) in order to improve the parameters of laser elements.

The efficiency of the formation of quasi-metallic defects in LiF, NaCl, KCl, and NaF crystals was investigated by optical spectroscopy. The conclusions about the nature of the centers, derived from the analysis of the processes of photo- and thermal transformations leading to their formation and destruction, are not unambiguous. The presence of a zero-phonon line (ZPL) is a favorable circumstance. For example, the temperature dependence of the total ZPL absorption can be used to determine the strength of coupling (S) of an electronic transition with lattice phonons. To this end, it is necessary to plot the functional dependence $f(x)$:

$$\ln(I_0/I) = f(-S(1 + 2\pi^2T^2/3\theta_D^2)),$$

where T is the measurement temperature and θ_D is the Debye temperature. The slope of this dependence, plotted in the above-mentioned coordinates, will determine the coupling strength S of the electronic transition. It follows from the exponential decrease in the ZPL intensity that

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

where I_0 is the ZPL intensity and I is the intensity in the integrated absorption band. The crystals were irradiated with γ photons (doses from 2.58×10^4 to 1.29×10^5 C/kg) and subjected to optical bleaching by either integrated light of xenon lamps in the quantron of a KVANT-17 laser or mercury lamp light transmitted through an UFS-2 light filter to form quasi-metallic defects.

Table 1. Efficiency of formation of quasi-metallic defects in the AHC series; the suggested order in the efficiency of defect formation is given in parentheses

Crystal	KI	LiF	KCl	NaF	NaCl	CsBr
$X^-/D\Delta$, 1/Å	4033 (1)	1513 (2)	456 (4)	339 (5)	750 (3)	31 (6)
X^-/D	726	333	260	190	60	17.8
Δ, Å	0.18	0.22	0.57	0.56	0.08	0.57

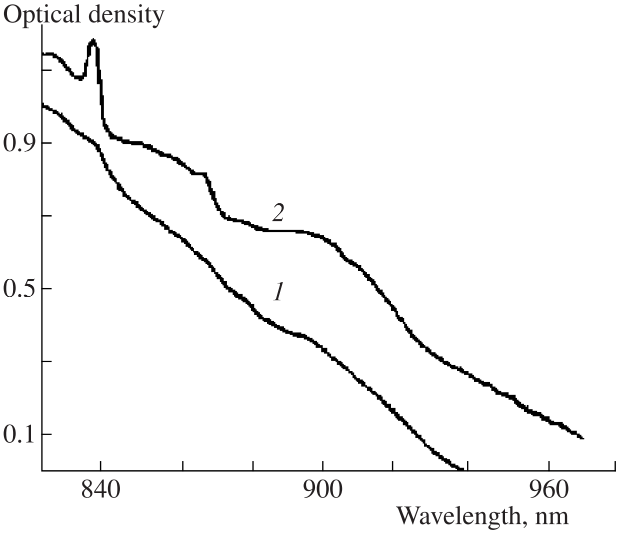

Fig. 1. Absorption spectra of a γ-irradiated NaCl crystal (dose 2.58×10^4 C/kg), recorded at temperatures T = (*1*) 80 and (*2*) 17 K.

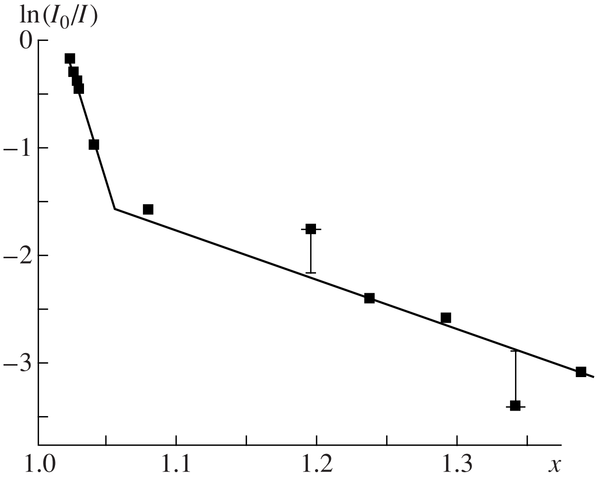

Fig. 2. Dependence of $\ln(I_0/I)$ on the variable $X = 1 + 2\pi^2T^2/3\theta_D^2$ for the 839.5-nm ZPL; the sample is γ-irradiated (2.58×10^4 C/kg) and optically bleached in the quantron of a KVANT-17 laser (n = 10 pulses); θ_D = 275 K.

It is known that the sizes of a halide atom and the stability of H centers affect the radiative processes and yield of defects. The smaller the ratio of the size X^- of a halogen ion to the size D of an interstitial site, the lower the yield [6]. If we consider quasi-metallic defects, we must also take into account the difference Δ between the metal atom and anion sizes (Table 1). Analysis of Table 1 shows that consideration of the efficiency of formation of quasi-metallic centers in the AHC series should be started with potassium iodide. However, this crystal is unstable due to the high activity of iodine.

QUASI-METALLIC CENTERS IN LiF CRYSTALS

The absorption spectra measured at T = 78 K in the N region (500–550 nm) contain 513.5- and 520.06-nm ZPLs. The obtained values of the parameter S are 2.04–2.17 for the 513.5-nm ZPL and 2.47–2.76 for the 520.06-nm ZPL.

Comparing these values with those for other color centers (Table 2), we can conclude that the recorded ZPLs are not due to F_4 centers, for which $S \sim 1$. The obtained values are closer to the coupling strength of quasi-metallic centers (S = 2.36–2.97) based on F_L defects [7].

N REGION IN THE SPECTRUM OF NaCl CRYSTALS

Previously, a vibrational structure has been observed in the N region of the spectrum (800–860 nm) with ZPLs at 837.5 (N_1) and 869.1 nm (N_2). However, the temperature dependence of the ZLP behavior was not measured and the coupling strength for an electron and lattice phonons was not estimated. Figure 1 shows the absorption spectrum of a γ-irradiated NaCl crystal (dose 1.29×10^5 C/kg) with induced quasi-metallic defects. At T = 17 K, the 839.5-nm ZPL is observed. The temperature dependence of $\ln(I_0/I)$ for a NaCl crystal exhibits two straight-line segments (Fig. 2) in the low-temperature region (with the parameter S = 41.2) and in the high-temperature region (with S = 5.08). At low temperatures, the experimental values fit well the straight line, while at high temperatures the straight line is plotted with some error (δ = 18%). This error is due

Table 2. Coupling strength for electronic transitions and lattice phonons

Center type	Crystal	I_0/I (T = 0 K)	S	Reference
$N_1(F_4)$	LiF	~0.37	~1	[8]
$R_2(F_3)$	LiF	0.02	3.9	[8]
$R_2(F_3)$	KCl	0.03	3.5	[8]
F_2^-	LiF	0.03	3.5	[8]
F_3^+	NaF	0.005	5.3	[8]
$M(F_2)$	LiF	$\sim 3 \times 10^{-4}$	8	[8]
F	LiF	$\sim 10^{-17}$	40	[8]
F_2F_L	LiF	–	2.36–2.97	[7]
ZPL 513.5 nm	LiF	-	2.04–2.17	
ZPL 520.06 nm	LiF	–	2.47–2.76	
ZPL 839.5 nm	NaCl	–	2.54×2	

to the fact that coupled modes are disregarded. It is known that the parameter S does not change much during a transition to another host. In [8], a change in the coupling strength by factor of 2 was reported. Then, we can suggest that defects with weak coupling ($S = 5.08/2 = 2.54$, $\theta_D = 275$ K) manifest themselves in the high-temperature region. This coupling is close to that of electrons with lattice phonons of quasi-metallic centers (Table 2) observed in LiF crystals [7]. In the low-temperature region, a defect with strong coupling manifests itself ($S = 41.2/2 = 20.6$). It may be a combination of two F centers in the $\langle 112 \rangle$ direction (as was believed in [9]). We are interested in the defect manifesting itself in the high-temperature region. Thus, quasi-metallic defects are formed in NaCl crystals under the action of ionizing radiation and subsequent optical and thermal treatments. Due to the classical configuration of F_3 and F_3^+ centers, favorable conditions arise for localization of an electron at the nearest regular cation, with simultaneous capture of the formed sodium atom by one of three (in case of F_3 centers) or two (in case of F_3^+ centers) under the action of light, heat, and radiation.

Taking into account the ion sizes, we can suggest that such defects are not formed in crystals characterized by a large difference between the metal atom and anion sizes, for example, in KCl ($\Delta = 0.57$ Å) and NaF ($\Delta = 0.56$ Å). Indeed, in KCl crystals, even at $T = 2$ K, ZPLs are not observed in the N region (960–1020 nm). ZPLs are neither observed in the N region (550–650 nm) and in the spectra of NaF crystals recorded at liquid-helium temperature.

Thus, the following regularity of the formation of quasi-metallic defects has been established: the efficiency of formation of quasi-metallic defects on the basis of F_L centers (an F_L center is a metal atom in an F center) in the AHC series depends on the difference in the sizes of the anion and alkaline metal atom. The smaller this difference and the larger the ratio of the anion size to the size of interstitial site, the higher the probability of the formation of quasi-metallic defects.

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