Optical Properties of Sodium Fluoride Crystals, Activated by Ytterbium

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Abstract – The influence of ytterbium and uranium on the optical properties of crystal NaF has been studied. In the infrared spectrum, when activating agents are added, the absorption bands increase: 2920, 2360 cm⁻¹ and so on. The change of a number of formed F- and M- color centers under the exposure to X-ray has been studied. It has been shown that the above impurities facilitate the accumulation of centers. In the thermoluminescence spectra the new thermal peaks specified by impurity-vacancy dipoles have been found out.

NaF, NaF-Yb and NaF-U,Yb crystals were grown in the air in a platinum cup by Cyropulos method from the reagent of particular purity. Ligands were introduced into the charge mixture before growing the crystal in the form of uranium nitrate $UO_2(NO_3)_2$ and ytterbium bromide $YbBr_3$ and were mixed thoroughly. The spectral analysis of samples has shown that in doped crystals the content of uranium is 0.01 % by weight. Ytterbium was 0.01 and 0.005 % by weight for crystals NaF-0.2Yb and NaF-0.1Yb, respectively. The X-ray exposure was carried out under 80K at the device URS-70 with tungsten X-ray tube 1BPV1 – 60 with vanadium anticathode (55 kilovolt, 10 `milliampere) through the aluminum plate 0.5 mm thick. The heating rate was kept fixed – 10 K/min.

When ytterbium is added, the absorption peaks in infrared spectrum (for which hydroxyls OH⁻ are responsible) are reduced and absorption peaks increase at 2920, 2850, 2360 and 2336 cm⁻¹ (Fig. 1). Complexes containing metals are apparently responsible for them.

In the work [1] there proposed two models of center for trivalent lanthanides in sodium bromide. In the first model the excess charge of Dy^{3+}, Ho^{3+} and others is compensated at the expense of two vacancies of sodium ions and in the second one – at the expense of impurity ions of oxygen which replace the ions of bromine. In our case ions of ytterbium which have radius (1.07 Å) compared to sodium (1.02 Å), are easily built into the lattice in divalent or trivalent condition. For charge compensation one or two cation vacancies appear next to ion. Another variant – replacement of one-two neighboring atoms of fluoride by atoms of oxygen. Apparently, in real crystals both possibilities are realized.
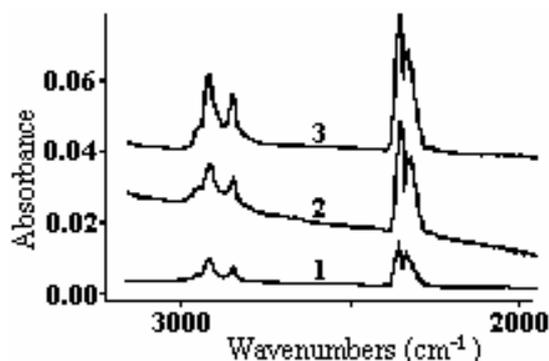

Fig. 1. Crystals' absorption spectra
1 – NaF, 2 – NaF-0.1Yb, 3 – NaF-0.2Yb

There has been studied the influence of Yb impurity on the processes of formation of F- and M-color centers in crystals NaF. There are different mechanisms of kinetic curves' description (for example [2] and others). We have proposed the model which takes into consideration not only formation, but also destruction of centers during X-ray [3]. Experimental curves of accumulation we decomposed into three components according to the formula:

$$f(t) = n_1(1 - e^{-b_1 t}) + n_2(1 - e^{-b_2 t}) - n_3(1 - e^{-b_3 t}).$$

The physical meaning of the first summand is the accumulation of centers in pre-radiation vacancies (the quick phase), and of the second one – their accumulation in newly formed vacancies (the slow phase). The third summand characterizes the disappearance of centers during X-ray. Parameters n_1 and n_2 – are the utmost obtainable levels of formation, and n_3 – destruction of centers; b_1, b_2, b_3 – are the speed parameters of formation and disappearance of centers. According to the formula, kinetic curves of centers' accumulation were decomposed into three components with estimation of numerical values of six parameters. Decomposition was conducted by least-squares method in the environment Matlab 6.5 using the built-in techniques for estimation of minimum of function of several variables. The obtained solutions are stable to variations of initial approximations of parameters. The example of decomposition is shown in Fig. 2.
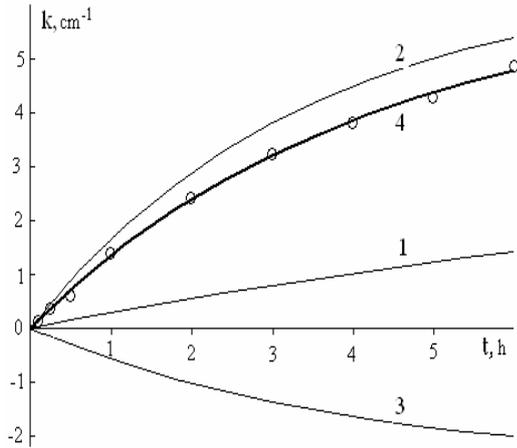
Fig. 2. Kinetics of accumulation of F-bands in the crystal NaF-Yb. Dots – experimental data, 1 – quick accumulation phase, 2 – slow phase, 3 – destruction phase, 4 – sum of three curves

It is seen that experimental data well coincide with calculation data. Parameters found by this formula are brought together in Tables 1 and 2. By comparing parameters n_i (k, cm^{-1}) and b_i (h^{-1}) for different kinetic curves, we may make a conclusion on processes occurring in crystals during irradiation.

In X-rayed crystals of NaF-Yb the number of F- and M-color centers (7,9) and the speed of their accumulation (3,77) at the initial stage is larger than in pure crystals of NaF (6,7). The same thing is observed for accumulation of M-centers. Under the increase of impurity concentration these parameters grow as well. This testifies that ions of ytterbium when entering the lattice create cation vacancies which facilitate the formation of electron color centers.

Table I. Parameters of kinetics of accumulation
   of F-bands

	n_1	b_1	n_2	b_2	n_3	b_3
NaF	6,7	3,51	22,1	0,37	15,2	0,05
NaF-0.1Yb	7,9	3,77	19,2	0,67	5,3	0,69
NaF-0.2Yb	13,1	1,98	16,8	0,07	6,0	0,36
NaF-U,0.2Yb	8,3	0,76	10,8	0,15	3,2	0,69

When two impurities are introduced, the number of pre-radiation vacancies reduces, since the parameter n_1 is smaller for the curve of NaF-U,0.2Yb crystal (8.3 and 1.4 for F- and M-centers, respectively), than for crystal of NaF-0.2Yb.

The high speed of accumulation of centers during the quick phase shows that in pure and poorly doped crystals F-centers are formed more effectively.

Parameter b_2, characterizing the speed of F-centers formation in undisturbed lattice, takes on the maximal value for crystals of NaF and NaF-0.1Yb. M-centers, conversely, are better formed in strongly doped crystals, though their number is small.

The last two parameters characterize the stability of formed centers. The number of destroyed F-centers in pure crystal (15.2) is maximal, though they are destroyed slowly (0.05). This testifies that they more stable in pure than in impurity crystals. M-centers are the least stable to crystals of NaF-0.1Yb and NaF-U,0.2Yb, as the coefficient of destruction for them is the largest ($b_3 = 0.84$ and $b_3 = 1.40$ respectively).

Table II. Parameters of kinetics of accumulation
   of M-bands

	n_1	b_1	n_2	b_2		
NaF	6,4	0,52	5,4	0,15		0,73
NaF – 0.1Yb	6,6	0,29	4,4	0,06	2,6	0,25
NaF – 0.2Yb	12,7	0,73	1,5	0,12	10,0	0,84
NaF-U,0.2Yb	1,4	0,22	1,9	0,31	0,5	1,40

There have been studied the thermoluminescence centers of crystals X-rayed at 80K. Ytterbium as many other rare-earth elements is a damper of luminescence, that is why, when Yb is added, the intensity of thermoluminescence peaks reduces.

Despite of this, in NaF-Yb crystals thermal peaks appear at 230 and 260 K. Thermal peak at 230 K is not found at the thermoluminescence of NaF crystals – both pure or with other impurities. Its intensity grows in parallel with the increase of ytterbium concentration. When uranium is added as a co-activating agent, this maximum a little bit increases. Peak at 260 K in NaF-U,Yb crystals increases by several hundred times. Obviously, it is caused by impurity-vacancy dipoles containing the ions of ytterbium.

Thus, ions of ytterbium are included into the lattice points of sodium fluoride, creating new centers by this. These centers change the absorption and luminescence spectra, influence on the processes of electron color centers' formation.

References
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