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## Abstract

## Full Text

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# OPTICAL AND LASER PROPERTIES OF MIXED $CdF_2$–$YF_3$ CRYSTALS ACTIVATED BY $Nd^{3+}$ IONS

*(Presented by Academician N. V. Belov, April 7, 1969)*

Among the large number of active media for optical quantum generators (OQG), fluoride crystals occupy a special place. Among them, crystals of the fluorite type ($MeF_2$, where Me = Ca, Sr, and Ba), activated by rare-earth ions (RE) ([1],[2]), have attracted and continue to attract the greatest attention of researchers. The results of their comprehensive study (spectroscopy, magnetic resonances, quantum electronics, X-ray phase analysis, etc.) have made it possible to obtain valuable information on the physics of the processes occurring in them under various conditions. Especially fruitful have been the studies carried out with their help to determine possibilities for improving the efficiency of active media for OQG. One path led to the discovery of a new class of working substances—mixed-type crystals (solid solutions)—on the basis of which about three dozen OQG have already been created ([2]). The present work is a continuation of a series of studies of mixed fluoride systems, in which cadmium fluoride ($CdF_2$) was chosen as the matrix material. This crystal interested us because OQG have not yet been created on its basis with $RE^{3+}$ ions as impurities, and the optical properties of its activator centers (a.c.) with $RE^{3+}$ ions have practically not been studied.

**Fig. 1.** Change in the unit-cell parameter of the $CdF_2$ solid-solution unit cell as a function of the $YF_3$ concentration (for the saturated solution $a_0 = 5.463$ Å)

Cadmium, being in the secondary subgroup of group II of the periodic system, has an outer-electron-shell configuration different from that of Ca, Sr, and Ba

($4d^{10}5s^2$). The presence of the $4d$ shell accounts for the strong polarizing action of the $Cd^{2+}$ ion. The more covalent character of the Cd–F chemical bond leads to the appearance in $CdF_2$ of a number of interesting physical properties not observed in $CaF_2$, $SrF_2$, and $BaF_2$. Cadmium fluoride is usually assigned to the structural type $CaF_2$ (space group $Fm3m$) ([3]). However, most works on the study of the structure of $CdF_2$ (performed on powder diffraction patterns) assign to it a space group different from that of $CaF_2$, namely $F43$ (for example, ([4])). Since structural studies of $CdF_2$ single crystals have not been carried out, the question of its space group cannot be regarded as definitively resolved; however, the data currently available indicate a difference between the structures of $CaF_2$ and $CdF_2$. An extremely interesting circumstance is also that $CdF_2$, after special treatment, acquires semiconducting properties ([5]). This enabled the authors of work ([6]) to record electroluminescence of certain $RE^{3+}$ ions. The unique combination in $CdF_2$ of a number of interesting physical properties with ne-

···undoubtedly shows that its comprehensive study is highly topical.

Our attempts to obtain induced emission in an OQG based on $CdF_2 - Nd^{3+}$ crystals at 300° K have so far been unsuccessful. Preliminary spectroscopic studies of these crystals showed that, already at an active-impurity concentration of 0.1–0.5 wt.%, strong concentration quenching of luminescence occurs. In comparison with $CaF_2$ crystals, in $CdF_2$ at equally small contents of $Nd^{3+}$ ions (less than 0.1 wt.%) a considerably larger absorption coefficient is recorded.

An analysis of the experience we have accumulated in studying the optical and generation properties of mixed crystals based on fluorides showed that the "laser efficiency" of simple crystals (7) and, in particular, $CdF_2$ with $TR^{3+}$ can be improved by searching for and synthesizing, on their basis, mixed systems with a disordered structure, characterized by a variety of absorption centers. Such studies were undertaken in our laboratory; their results led to the creation of an OQG based on mixed $CdF_2 - YF_3 - Nd^{3+}$ crystals, generating at 300° K with a sufficiently low excitation threshold $E_p$.

Since the phase diagram of the $CdF_2 - YF_3$ system had not been investigated, the preparation of "mixed single crystals" was preceded by a study of the stability region of cubic solid solutions. The results of X-ray phase analysis and determination of unit-cell parameters, carried out on an AFV-201 diffractometer with Cu $K_{\alpha1,\alpha2}$ ($\lambda_{\mathrm{Cu}\ K_{\alpha1}} = 1.5405$ Å), are shown in Fig. 1. It is seen that isomorphous substitution of $Cd^{2+}$ ions by $Y^{3+}$ occurs over a wide range of compositions, with a limiting concentration of the solid solution of $YF_2$ in $CdF_2$ of $30.5 \pm 1$ mol.%. For generation experiments, $CdF_2 - YF_3 - Nd^{3+}$ single crystals of average optical quality (throughout the entire volume there were striae and blocks) were used, synthesized by the Stockbarger method in a fluorinating atmosphere (8). The content of $YF_3$ in them was varied from 5 to 20 wt.%, and that of $NdF_3$ from 0.5 to 2 wt.%. Composition control was carried out by determining the unit-cell parameters.

Fig. 2

Figure 2: Fig. 2

Fig. 3. Spectrum of induced radiation of an OQG based on a $CdF_2$—$YF_3$—$Nd^{3+}$ crystal at 300° K. The arrow marks the reference line with $\lambda = 10561.5$ Å.

Figure 3: Fig. 3. Spectrum of induced radiation of an OQG based on a $CdF_2$ —$YF_3$—$Nd^{3+}$ crystal at 300° K. The arrow marks the reference line with $\lambda = 10561.5$ Å.

**Fig. 2.** Luminescence spectra corresponding to the transition ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ of crystals: $CdF_2 - YF_3 - Nd^{3+}$ at 300° K (a), $CdF_2 - YF_3 - Nd^{3+}$ at 77° K (b), and $CdF_2 - Nd^{3+}$ at 77° (c). $\lambda_g$ denotes the generation wavelength of an OQG based on the mixed crystal at 300° K.

Induced emission at 300° K was obtained in an OQG consisting of an illuminating system (a cylinder of elliptical cross section) with an ISP-1000 xenon lamp and external spherical mirrors ($R = 576$ mm) with multilayer dielectric coatings (at $\lambda = 1.06\,\mu$, $\tau = 0.7\%$), mounted confocally. Thus, for example, a $CdF_2 - YF_3$ ($\sim 15$ wt.%)-$Nd^{3+}$ ($\sim 2$ wt.%) crystal, located in a tubular filter made of ZhS-17 glass, at 300° K had $E_p \simeq 12$ J (length 23 mm, diameter 6 mm, plane-parallelism of the end faces 20″). Spectroscopic···

studies of the induced radiation, carried out on a DFS-8 diffraction spectrograph ($\sim 5.9$ Å/mm), showed that $\lambda_g$ of this OQG is $10651 \pm 7$ Å (9389 $cm^{-1}$), with an emission-line width $\Delta\nu_g \cong 19$ $cm^{-1}$ at $E_{exc} = (3—5) \cdot E_{th}$ and above. The generation spectrum obtained at 300° K is shown in Fig. 3.

**Fig. 3.** Spectrum of induced radiation of an OQG based on a $CdF_2$—$YF_3$—$Nd^{3+}$ crystal at 300° K. The arrow marks the reference line with $\lambda = 10561.5$ Å.

The luminescence spectra (the transition ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$) of $CdF_2$—$YF_3$ ($\sim 15$ wt.%)—$Nd^{3+}$ ($\sim 0.5$ wt.%) and $CdF_2$—$Nd^{3+}$ (0.03 wt.%) crystals, obtained at 77 and 300° K on a DFS-12 spectrometer, are shown in Fig. 2. As can be seen, at room temperature the width of the luminescence band (at the 0.5 level) of the $CdF_2$—$YF_3$—$Nd^{3+}$ crystal is about 270 $cm^{-1}$. Measurement of the lifetime of the excited state of $Nd^{3+}$ ions (${}^4F_{3/2}$) at 300° K in $CdF_2$—$YF_3$ ($\sim 15$ wt.%) —$Nd^{3+}$ ($\sim 2$ wt.%) crystals showed that it is equal to $310 \pm 20$ $\mu$s.

*Note added in proof.* At 300° K, induced radiation was also obtained in OQGs based on $CdF_2$—$LaF_3$—$Nd^{3+}$ and $CdF_2$—$YF_3$—$LaF_3$—$Nd^{3+}$ crystals.

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*Note: Figure translations are in progress. See original paper for figures.*