

Luminescence properties of NaAlP_2O_7 crystals doped with chromium ions

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Luminescence properties of NaAlP_2O_7 crystals doped with chromium ions have been investigated. Luminescence spectra of these crystals consist of two main bands in the green-orange and red spectral regions, respectively. Positions and shapes of the bands depend on the sample temperature, concentration of the impurity ions, and excitation wavelength. Complex structure of the green-orange band is caused by a superposition of matrix intrinsic radiation and emission of the distorted CrO_4^{2-} groups, where chromium ion has 6+ charge. The red luminescence band was assigned to electron transition in the Cr^{3+} ions located in the octahedral oxygen environment. A special attention has been paid to discuss the possibility for chromium ions arrangement in different positions of the crystal lattice.

Рассматриваются люминесцентные свойства кристаллов NaAlP_2O_7 , активированных ионами хрома. Спектры люминесценции этих кристаллов состоят из двух основных полос, расположенных соответственно в зелено-оранжевой и красной областях спектра. Положение полос и их форма зависят от температуры кристалла, концентрации примеси и длины волны возбуждающего излучения. Сложная структура зелено-оранжевой полосы обусловлена суперпозицией излучения матрицы кристалла и примесных ионов хрома в зарядовом состоянии 6+, которые входят в состав групп CrO_4^{2-} . Красная полоса люминесценции обусловлена электронными переходами в ионах Cr^{3+} в октаэдрическом кислородном окружении. Обсуждаются возможности вхождения ионов хрома в разные позиции решетки кристалла.

Despite of numerous laser-active solid materials being applied in modern laser engineering, there is a continuous need to develop new laser-active working media for such lasers. There are some main directions for such developments: providing the light generation in new optical spectral regions, providing a continuously frequency-tuned generation in new regions, working out of new sensitization schemes of active impurity ions. Chromium ions are well known as active emitting impurity as well as sensitizing one [1–3]. Oxide crystals and glasses have the advanced place among the laser matrices, because they does not loss their optical quality at high concentration levels of the impurity chromium ions, at the same time, the concentration quenching is insignificant, therefore, these matrixes are used

widely to manufacture the lasers. Numerous works are devoted to investigation of spectroscopic properties of such materials doped with chromium ions, but some important matters concerning the light absorption and emission processes are still unclear [4–6]. In particular, there is a question about formation of various types of luminescence centers, different possibilities for chromium ions to have got one of charge states (Cr^{3+} , Cr^{4+} and Cr^{6+}), about arrangements of chromium ions in various positions in the crystal lattices.

This paper presents the investigation results of NaAlP_2O_7 double sodium-aluminum phosphate crystals doped with chromium ions in various concentrations. The lattice of these crystals allows isovalent substitution of Cr^{3+} chromium impurity ions for

Al^{3+} aluminum ones in the lattice. Besides, as it will be shown below, a principal possibility exists for arrangement of chromium ions in their various charge states in matrix of the double sodium-aluminum phosphate. This property is very important for varying the spectral and luminescence properties of the doped matrix in a wide range.

Polycrystalline NaAlP_2O_7 samples were synthesized from a melted mixture of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ oxides of Chemically Pure grade. The activating chromium ions were incorporated into the samples by adding Cr_2O_3 oxide to the above-mentioned mixture. The Cr_2O_3 concentrations ($C(\text{Cr})$) in the mixture were 0.02, 0.08, or 1 % (mass). The samples obtained after drying were finely dispersed powders or composites of single crystals of about $2 \times 1 \times 1 \text{ mm}^3$ size.

Luminescence properties of the NaAlP_2O_7 crystals were investigated at 4.2, 77, and 300 K. The samples were cooled in liquid helium and nitrogen cryostats at 4.2 and 77 K, respectively. The ILGI-501 (excitation wavelength $\lambda_{ex} = 337.1 \text{ nm}$), LGN-503 ($\lambda_{ex} = 476.5, 488.4, \text{ and } 514.2 \text{ nm}$), and LG-22 ($\lambda_{ex} = 632.8 \text{ nm}$) lasers were used to excite the luminescence. The luminescence excitation spectra were studied using DXeEl-1000 xenon lamp in a 300–650 nm wavelength range. The radiation spectrum was measured using a double prism spectrometer DMR-4. A DFS-12 spectrometer (reciprocal linear dispersion 10 \AA/mm) was used to record the luminescence spectra.

The double phosphate sodium aluminum crystals doped with chromium ions ($\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals) reveal an intense luminescence in the essentially whole visible region under 300–650 nm ($33300\text{--}15400 \text{ cm}^{-1}$) excitation. The luminescence spectra consist of two bands. At the sample temperatures $T = 4.2$ to 77 K, there are "green-orange" short-wavelength band in the 450–650 nm region with the main maximum near $\lambda_m \sim 525$ to 575 nm and "red" long-wavelength one in the 700–800 nm region with the maximum near $\lambda_m = 734$ to 737 nm. The maxima positions depend on the impurity ion concentration, sample temperature, and excitation wavelength.

Excitation spectra of the "red" luminescence band of $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals consist of two wide bands in the 550–700 nm ($18180\text{--}14300 \text{ cm}^{-1}$) (band I) and 380–525 nm ($26300\text{--}19000 \text{ cm}^{-1}$) (band II) spectral regions and one low-intensity band in the 280–350 nm ($35700\text{--}28600 \text{ cm}^{-1}$) (band

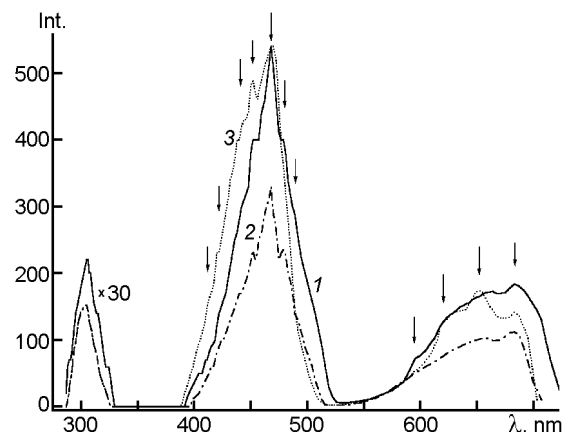


Fig. 1. Excitation spectra of chromium doped $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals. ($C(\text{Cr})$, % mass: 0.08 (1, 3) and 0.02 (2)), obtained at temperature (K): 300 (1, 2) and 77 (3); registration wavelength $\lambda_r = 735 \text{ nm}$.

III) ultra-violet region with the main maximum at $\lambda_m = 300 \text{ nm}$ (Fig. 1). Change of chromium ion concentration from 0.02 to 0.08 % (mass) does not influence essentially the excitation spectra of the "red" luminescence band. The number and position of the peaks remain essentially unchanged. Effect of temperature on the excitation spectra has some specific features. This effect reveals itself in a change of the components intensity ratio within the I and II bands of the excitation spectra. Specifically, temperature elevation from 4.2 to 300 K results in increasing relative intensity of the short-wavelength components in both excitation bands. We assume that the main radiation transitions which excite the impurities occur at the next wavelengths with maxima λ_m (wave numbers ν_m) in the excitation spectra (peak positions are pointed by arrows in the excitation spectra): the band III — 290 (34500), 300 (33000), and 315 nm (31750 cm^{-1}); the band II — 413 (24200), 422 (23700), 442 (22620), 452 (22120), 468 (21370), 479 (20900), and 481 nm (20800 cm^{-1}); the band I — 595 (16800), 623 (16050), 658 (15200), and 683 nm (14650 cm^{-1}). As it will be shown below, the long-wavelength band in the "red" luminescence excitation spectra is caused by the light interaction with the impurity chromium ions.

Let us consider in more detail the luminescence spectra of the $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals doped with chromium ions as depending on temperature, the impurity ion concentration, and excitation wavelength. As it was mentioned above, the emission of the doped

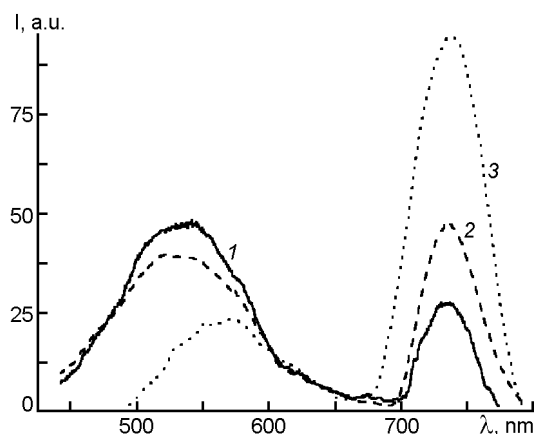


Fig. 2. Luminescence spectra of $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals ($\text{C}(\text{Cr}) = 0.08\%$ mass) at excitation wavelength $\lambda_{\text{ex}} = 337.1$ nm and temperature $T = 4.2$ (1), 77 (2) and 300 K (3).

crystals consist of two bands, the "green-orange" short-wavelength and the "red" long-wavelength ones. The short-wavelength band consists no doubt of several poor-resolved structural components. In fact, asymmetric band shape and spectral features are revealed in its structure $\lambda \sim 475$, 517, 545, 575, and 625 nm confirm the decreasing short-wavelength components intensities of the luminescence band as the temperature increases. So, the component peaked at 475 nm is absent at $T = 300$ K (Fig. 2). Temperature changes result in relative intensity changes of the "green-orange" and the "red" bands, luminescence intensity of the latter one essentially increases with the temperature increase. Intensities of the long-wavelength components in the "green-orange" band rise essentially as the chromium ion concentration in the sample increases. As a result, this band contour maximum becomes shifted to the long-wavelength region.

Now let the luminescence spectra properties depending on the excitation wavelength be considered in more detail. As it was mentioned above, the "red" luminescence band is induced by the excitation within limits of each excitation band (bands I, II, III). Only this band is observed in the luminescence spectra at the most long-wavelength excitation (band I). The shape of this band depends on the sample temperature. The band is narrowed and some shoulders arise against the background of its short-wavelength wing in the region 700–725 nm when temperature decreases from 300 to 4.2 K. These shoulders can be a manifestation of some fine structure components. The

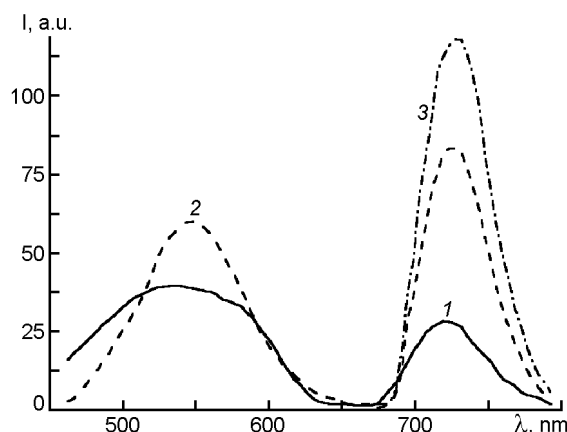


Fig. 3. Luminescence spectra of $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals ($\text{C}(\text{Cr}) = 0.08\%$ mass) at $T = 77$ K and $\lambda_{\text{ex}} = 337.1$ (1), 488.4 (2) and 632.8 nm (3).

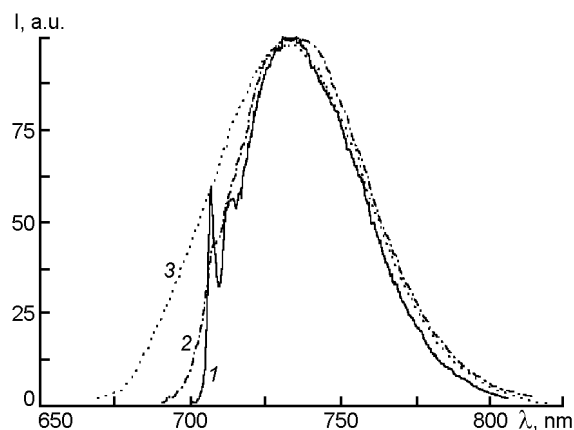


Fig. 4. Luminescence spectra of $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals ($\text{C}(\text{Cr}) = 0.08\%$ mass) at excitation wavelength $\lambda_{\text{ex}} = 632.8$ nm and $T = 4.2$ (1), 77 (2) and 300 K (3).

latter are observed at $\lambda_{\text{ex}} = 632.8$ nm as one sharp peak at $\lambda_m = 707$ nm and a low-intensity shoulder located near 713 nm (Fig. 3,4). The long-wavelength components of the short-wavelength band appear near the "red" luminescence band at the excitation within limits of the medium band II (530–680 nm region). And only excitation within the most short-wavelength band III of the excitation spectra (280–350 nm region) induces both the "green-orange" and the "red" luminescence bands (Fig. 2,3).

The described results show that both doped and undoped NaAlP_2O_7 crystals exhibit luminescent properties. Before, we investigated the luminescence properties of similar pure and chromium-doped double potassium-aluminum phosphate KAIP_2O_7 crystals [14]. Luminescence properties of the both compounds are similar to one an-

other. The luminescence spectra of KAIP_2O_7 crystals include two bands, "green-orange" and "red" ones. Their positions and structures are similar to the corresponding bands of the NaAlP_2O_7 crystal luminescence spectra. The similar situation was observed in the excitation spectra of both samples. Therefore, taking into account the above observations and obtained experimental data, we can assume that the luminescence of the doped $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals is caused by matrix which generates its intrinsic emission as well as by impurity chromium ions responsible for emission of extrinsic luminescence centers formed therewith. The "blue-green" intrinsic matrix emission can be due to various causes. Some of those are inherent in the matrix while other ones caused by uncontrolled factors. At present, there are not enough experimental data to discuss the nature of this emission. As for chromium luminescence centers, the data on possible schemes of impurity chromium ion incorporation into the NaAlP_2O_7 crystal lattice and spectroscopy of chromium ions in oxide crystals are necessary to discuss the nature of emission of the impurity chromium luminescence centers in the investigated compounds.

It is just the three-dimensional network of AlO_6 octahedrons and P_2O_7 diphosphate groups bound with common oxide vertices that forms the structure base of the NaAlP_2O_7 crystal of monoclinic syngony. Each octahedron is bound with five diphosphate groups, one of those being attached with bidentate bond and four others, with bridge ones [7]. Sodium, aluminum and phosphorus ions of these compounds are positively charged and have +1, +3 and +5 charge, respectively. Taking into consideration the electric neutrality principle and the radii ratio of mentioned impurity and lattice ions, the Cr^{3+} chromium ions arrangement in the aluminum sites in the AlO_6 octahedrons can be assumed to be the optimum arrangement for these ions. In fact, the aluminum and chromium ions charges are the same (3+) and their radii are 0.053 and 0.062 Å, respectively (the radii ratio is $R(\text{Cr}^{3+})/R(\text{Al}^{3+}) = 1.17$ [1]), that is favorable enough for Cr^{3+} ion substitution for aluminum one in the NaAlP_2O_7 crystal lattice. The Cr^{3+} ion radius ratios to the sodium and phosphorus P^{5+} ionic radii are $R(\text{Cr}^{3+})/R(\text{Na}^+) = 6$ and $R(\text{Cr}^{3+})/R(\text{P}^{5+}) = 3.65$, respectively. Such values of the radii ratios are unfavorable for the chromium Cr^{3+} ion incorporation in the sodium and the phos-

phorus positions. But these possibilities are not to be eliminated completely, especially at high concentrations of the impurity ions. Possibility to displace the phosphorus ions seems more probable, as this case inquires only to compensate an effective charge -2 that is formed after such substitution. The compensation may occur due to formation of an oxide vacancy in the diphosphate group in the course of the doped crystal growth. Possibility for the chromium ion incorporation in the sodium position seems to be less probable, as these ions radii are very different. Besides, in this case, a complex compensation of an effective charge +2 needs to form vacancies of two neighbor sodium ions.

When considering the experimental data, it is to be taken into account that some natural and synthetic compounds contain chromium ions with +6 charge in tetrahedral oxide surrounding [8]. Real geometry of the tetrahedral groups does not exist in a perfect NaAlP_2O_7 crystal, but the P_2O_7 diphosphate groups of the crystals can be considered as those formed by two PO_4 tetrahedral groups containing one common oxygen ion. The phosphorus ion in these groups has four oxygen ions in the nearest neighborhood. That is why, the $\text{O}_3\text{-P-O}$ part of the diphosphate groups can be considered as a PO_4 tetrahedron deformed in geometry and in charge. Relation between the impurity Cr^{6+} and the P^{5+} ion radii is equal $R(\text{Cr}^{6+})/R(\text{P}^{5+}) = 1.76$ that is rather suitable for realization of the phosphorus ion displacement by the impurity Cr^{6+} one. Compensation of the +1 extra charge could occur in a very simple way: by one sodium atom vacancy.

So, consideration of the possible chromium ion incorporation variants into the NaAlP_2O_7 crystal lattice must take into account the Cr^{3+} ion incorporation as Cr^{3+} in the aluminum ion site and as Cr^{6+} in the phosphorus ion site in diphosphate with formation of the $\text{O}_3\text{-P-(O-Cr-O}_3)$ group. Surely the electronic structure of the (O-Cr-O_3) fragment in the mentioned group is far from the ideal free tetrahedron CrO_4^{2-} one but, on the other hand, as it was shown recently, just the deformed CrO_4 tetrahedrons containing the CrO_4^{2-} groups are responsible for photo- and X-ray luminescence of the oxide crystals [7, 9].

Indeed, when comparing the luminescence and the excitation characteristics obtained by us for the $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals with characteristics of CrO_4^{2-} molecular

groups present as impurities in various matrices (alkali halide crystals, crystals and glasses of alkali and alkali-earth halides [9, 10]) or as components of the complex oxide crystals (alkali and alkali earth chromate crystals, etc. [11, 12]), it is seen that the long-wavelength components of the "green-orange" luminescence could be related to the CrO_4^{2-} group emission. Accordingly to the same data, the CrO_4^{2-} chromate groups could be the base of the complex luminescence centers, emission of which is characterized by spectral bands in the 600–800 nm wavelength region. The mentioned complex luminescence centers are formed preferably in the crystals which contain some defects, e.g., oxygen vacancies, positively charged impurities, and F -centers as well.

As to spectroscopic characteristics of Cr^{3+} ions, their luminescence in a solid state can be revealed as a wide electron vibration band (${}^4T_2 \rightarrow {}^4A_2$ transition) and/or two narrow, so-called R -lines caused by ${}^2E \rightarrow {}^4A_2$ transitions. The latter, if any, have to lie at the short-wavelength side of the "red" luminescence band. The maxima of above-mentioned bands and lines lie in the region from 670 to 800 nm. The positions of lines and bands are defined by the crystal field force (by the crystal matrix type) where the Cr^{3+} ion is incorporated [2–5]. The experimental results concerning the chromium doped $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals could be explained as follows, taking into consideration the above concepts of the possible forms of chromium ion incorporation in the NaAlP_2O_7 lattice and possible manifestations of their luminescent properties in some solid matrices.

The "green-orange" emission of the deformed CrO_4^{2-} molecular groups in the chromium doped $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystals is accompanied by the intrinsic "blue-green" matrix emission. Luminescence of the complex centers formed on the base of the same molecular groups may cause in part the "red" luminescence of the doped crystals. It should be noted that the shape of "red" luminescence band differs from that of CrO_4^{2-} complex luminescence centers. Moreover, the low formation probability of these centers must be taken into account. That is why we tend to opinion that the $\text{NaAlP}_2\text{O}_7(\text{Cr})$ crystal "red" luminescence is caused by emissive transition in Cr^{3+} ions.

The concepts of complex superposition structure of the luminescence spectra (intrinsic matrix luminescence + Cr^{3+} impurity

emission + emission of the centers formed on the base of the CrO_4^{2-} molecular groups) make it possible to explain the changes in the luminescence spectra dependent on the temperature and the excitation wavelength. According to literature data, the short-wavelength excitation in the range of the excitation band I (particularly, at $\lambda_{ex} = 337.1$ nm) induces the matrix emission as well as that of the deformed CrO_4^{2-} molecular groups. Those compose together the "blue-green-orange" luminescence band [9–12]. That is why the latter contains a set of components (Fig. 2, 3). The light from the excitation band II region is unavailable to excite the intrinsic matrix emission, so the impurity luminescence bands only are observed. Those are caused by the emission of the CrO_4^{2-} deformed molecular groups, of the complex centers formed on their base, and by the Cr^{3+} emission. Changes in the shapes, relative intensities, and the maxima positions (Fig. 3) are related with changing contributions of specific centers to the total spectra, depending on the excitation wavelength.

Temperature changes taking place under the short (Fig. 2) and the long (Fig. 4) wavelength excitation differ in nature. It is to believe that temperature elevation at the short-wavelength excitation (particularly at $\lambda_{ex} = 337.1$ nm) initiates the excitation energy transfer from the matrix to Cr^{3+} -ions, thus causing intensity increase of the long-wavelength components of the "green-orange" luminescence band and rising the "red" luminescence band intensity as well (Fig. 2). Temperature changes of the "red" luminescence band occurring at the longest-wavelength excitation in the region of band I (particularly at $\lambda_{ex} = 632.8$ nm), when only the impurity Cr^{3+} ions can be excited (Fig. 4), are explained by temperature dependence of the electron-vibration interaction rate at the ${}^4T_2 \rightarrow {}^4A_2$ electronic transition. The "red" band narrows as the temperature decreases due to weakening electron-vibration interaction. As a result, the details of spectra masked before became visible; especially narrow lines of the ${}^2E \rightarrow {}^4A_2$ transitions become observable [4–6].

To conclude, the luminescence of chromium doped NaAlP_2O_7 crystals is a superposition of the intrinsic matrix emission and emission of luminescence centers formed by the impurity chromium ions. The "green-orange" luminescence band (450–690 nm region) is a superposition of the matrix lumi-

nescence (short-wavelength components at 475 and 517 nm) and emission of the distorted CrO_4^{2-} molecular groups, those cause the luminescence spectra components peaked near 545, 575, and 625 nm. The "red" luminescence band peaked near 736 nm as well as the narrow lines at 707 and 713 nm at its short-wavelength wing are generated by Cr^{3+} ions substituting Al^{3+} ones in the crystal lattice.

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Люмінесцентні властивості кристалів NaAlP_2O_7 , активованих іонами хрому

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Розглядаються люмінесцентні властивості кристалів NaAlP_2O_7 , активованих іонами хрому. Спектри люмінесценції цих кристалів складаються з двох основних смуг, які знаходяться у зелено-оранжевій та червоній областях спектру, відповідно. Положення смуг та їх форма залежать від температури кристала, концентрації домішки та довжини хвилі збуджуючого випромінювання. Складна структура зелено-оранжевої смуги пояснюється суперпозицією випромінювання матриці кристала та домішкових іонів хрому в зарядовому стані $6+$, що входять до складу групи CrO_4^{2-} . Червона смуга люмінесценції зумовлена електронними переходами в іонах Cr^{3+} в октаедричному кисневому оточенні. Обговорюються можливості входження іонів хрому в різні позиції ґратки кристала.