LUMINESCENCE SPECTROSCOPY OF KMP$_2$O$_7$ DIPHOSPHATE CRYSTALS (M = Al, In) DOPED WITH CHROMIUM IONS

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We considered luminescence properties of KMP$_2$O$_7$ (M = Al, In) crystals doped with chromium ions. The luminescence spectra of these crystals consist of two principal bands located in the green-orange and red spectral regions. The positions of the bands as well as their shape depend on the type of a metal (Al or In), the temperature of a crystal, the admixture concentration, and the exciting radiation wavelength. A complicated structure of the green-orange band results from a superposition of the radiation of the crystal matrix and that of admixture chromium ions in the charge state 6$^+$ that belong to CrO$_4^{2-}$ molecular groups. The red luminescence band is conditioned by radiative transitions in Cr^{3+} ions in the octahedral oxygen environment. We consider the influence of the crystal field strength on the position of the red luminescence band. The possibilities for chromium ions to occupy various sites of the crystal lattice are discussed.

1. Introduction

For today, a great number of materials are used for creating the active media of optical solid-state lasers, but there still remains a need for searching new working substances for them. The principal directions of the work in this field are the following: the lasing in new regions of the optical range, the lasing with a variable radiation wavelength, and the development of new schemes of sensitization of active impurities. Among impurities, both active generating ones and impurities-sensitizers, a dominant place is held by chromium ions, while the most appropriate matrices are oxide crystals and glass [1—6]. This is conditioned by the facts that oxide matrices don't lose their optical quality in the case of doping them with a large number of impurity chromium ions, and the attenuation of the concentration in them is inessential. The investigation of spectroscopic properties of such materials doped with chromium ions was carried out in a large number of papers, but several important questions concerning the processes of light absorption and radiation still remain unanswered [7 — 9]. In particular, this concerns the questions about the ways of the formation of luminescence centers of various types, the possibility for chromium ions to exist in various

charge states (Cr^{3+}, Cr^{4+}, Cr^{6+}), and the possibility to arrange chromium ions in various sites of the lattice.

The given paper is devoted to the investigation of double phosphates of the general form KMeP$_2$O$_7$, where Me = Al or In, with admixtures of chromium ions in various concentrations. The structure of these crystals enables the isovalent replacement of Al^{3+} or In^{3+} ions by admixture chromium ions Cr^{3+}. In addition, as will be shown below, there exists a fundamental possibility for chromium ions to exist in various charge states in the matrix of double phosphates under investigation. These properties are important for the variation of spectral-luminescent properties of admixture matrices in a wide spectral range.

2. Experimental Technique

Polycrystalline samples of KMeP$_2$O$_7$ (Me = Al, In) crystals were synthesized from a melt of the mixture of K$_2$O—Me$_2$O$_3$—P$_2$O$_5$ oxides of the "chemically pure" (ch.p) qualification. Activating chromium ions were introduced into the composition of the samples by means of adding Cr$_2$O$_3$ oxide to the mentioned mixture with its concentration in the mixture being equal to 0.02, 0.08, or 1 mass %. The samples after drying had the form of fine-dispersed powders.

The luminescence of KMeP$_2$O$_7$ (Me = Al, In) crystals was investigated at temperatures of 4.2, 77, and 300 K. The samples were placed into a helium or nitrogen cryostat where the temperature of the samples amounted to 4.2 or 77 K, respectively. The luminescence was excited with the radiation of an ILGI-501 (the wavelength of excitation λ_{ex} = 337.1 nm), an LGN-503 ((λ_{ex} = 476.5, 488.4, and 514.2 nm), and an LG-22 (λ_{ex} = 632.8 nm) lasers. The spectra of luminescence excitation were investigated using the radiation of a DKsEl-1000 xenon lamp (the range of excitation wavelengths is 300 — 650 nm). The spectral
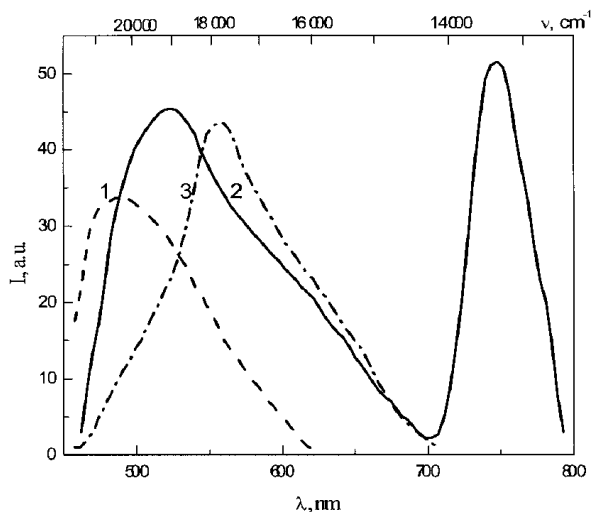
Fig. 1. Luminescence spectra of pure $KAlP_2O_7$ (1), $KAlP_2O_7$(Cr) ($C_{Cr} = 0.08$ mass%) (2), and $KInP_2O_7$(Cr) ($C_{Cr} = 1$ mass%) (3) crystals obtained at the temperature $T = 77$ K and the excitation wavelength $\lambda_{ex} = 337.1$ nm

Fig. 2. a — Luminescence spectra of $KAlP_2O_7$(Cr) ($C_{Cr} = 0.08$ mass%, $T = 4.2$ (1), 77 (2), and 300 K (3); $\lambda_{ex} = 337.1$ nm and the excitation spectrum of $KAlP_2O_7$(Cr) crystals ($C_{Cr} = 0.08$ mass%) (4) at $\lambda_p = 740$ nm, $T = 300$ K; b — Luminescence spectra of $KInP_2O_7$(Cr) crystals ($C_{Cr} = 1$ mass%), $T = 4.2$ (1), 77 (2), and 300 K (3), $\lambda_{ex} = 337.1$ нм; c — Luminescence spectra of $KAlP_2O_7$(Cr) crystals ($C_{Cr} = 0.02$ mass%) at $\lambda_{ex} = 337.1$ (1) and 488 nm (2), $T = 77$ K

decomposition of the radiation was carried out by a DMR-4 double prism monochromator. A DFS-12 spectrometer (with a reciprocal linear dispersion of 10 Å/mm) was used for recording the spectra of luminescence and luminescence excitation. The differential reflectance spectra (the spectra of chromium-doped samples with respect to those of undoped ones) were recorded with the help of a SPECORD M40 spectrometer.

3. Experimental Results

Under the influence of light with wavelengths λ_{ex} (frequencies ν_{ex}) of excitation lying in the region $300 - 650$ nm ($33000 - 15400$ cm^{-1}), the crystals of aluminum diphosphates doped with chromium ions, $KAlP_2O_7$(Cr), manifest the intensive luminescence practically in the whole visible range. The spectra of this emission consist of two bands: a short-wave green-orange one lying in the range $450 - 700$ nm and having a maximum of the envelope (λ_m) in the region $\sim 495 \div 550$ nm at a temperature of the samples $T = 4.2 \div 300$ K and a long-wave red one that lies in the range $700 - 800$ nm with a maximum of the envelope in the region $\lambda_m = 740 \div 750$ nm. The positions of these bands depend on the concentration of admixture chromium ions, the temperature of the samples, and the exciting radiation wavelength (Fig.1, Fig. 2,a). Under similar conditions
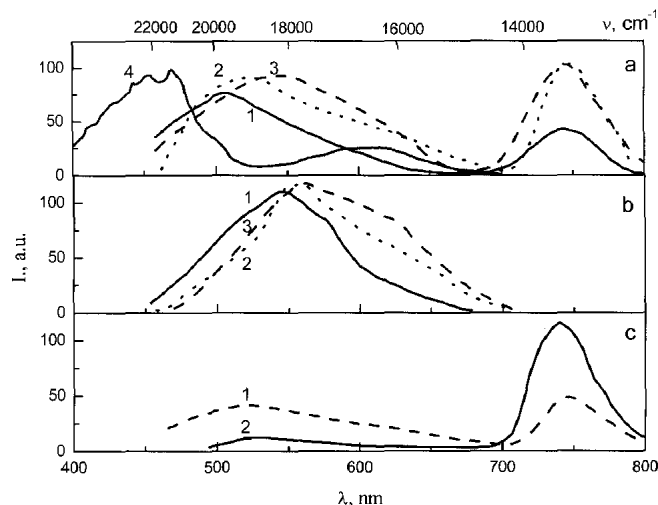
(excitation in the range $300 - 650$ nm and the temperatures of the samples $T = 4.2 \div 300$ K), indium diphosphate crystals doped with chromium ions $KInP_2O_7$(Cr) manifest the luminescence only in the short-wave green-orange band that lies in the wavelength region $450 - 700$ nm with a maximum of the envelope (λ_m) lying in the range $\sim 550 \div 570$ nm (Fig.1, Fig. 2,b).

In chromium-free "pure" $KAlP_2O_7$ crystals, there exists only a short-wave luminescence band lying in the range $450-600$ nm with the envelope maximum $\lambda_m \sim 490$ nm. In chromium-doped crystals, the long-wave edge of this band intensifies, and new additional components appear in the range $550-700$ nm (Fig. 1, curves 1, 2). Thus, the green-orange luminescence band of $KAlP_2O_7$(Cr) crystals can be considered as one formed due to the superposition of three wide components, where the middle component having a maximum at $\lambda_m = 545$ nm is most intensive at room temperature (Fig. 2,a). With increase in the content of chromium C_{Cr}, the intensity of long-wave components of the green-orange band for double aluminum phosphates rises, and, as a result, the maximum of the envelope of this band shifts towards the long-wave side. Moreover, the ratio of the intensities of the green-orange and red bands for $KAlP_2O_7$(Cr)

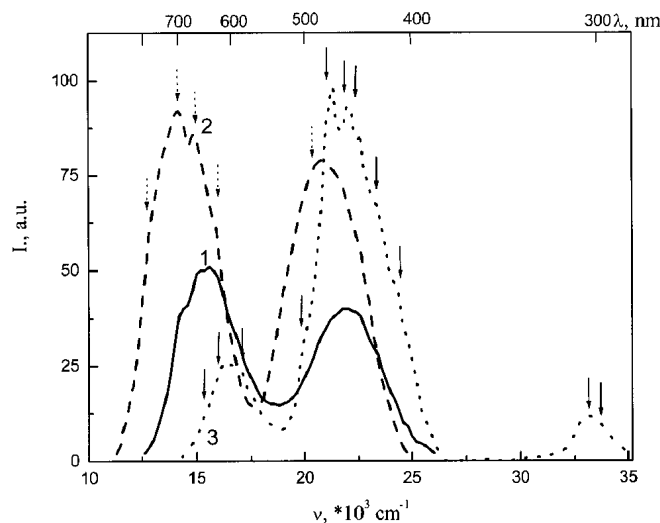Fig. 3. Reflectance spectra of crystals $KInP_2O_7(Cr)$ ($C_{Cr} = 1$ mass%) (1), $KAlP_2O_7(Cr)$ ($C_{Cr} = 0.08$ mass%) (2), $T = 300$ K and the excitation spectrum of $KAlP_2O_7(Cr)$ crystals ($C_{Cr} = 0.08$ mass% (3), $\lambda_p = 740$ nm and $T = 300$ K

crystals also changes: for larger C_{Cr}, the relative intensity of the red band increases.

The luminescence band of $KInP_2O_7(Cr)$ crystals is complicated and can be also considered as a result of the superposition of three components (Fig. 2, b).

A reduction of the temperature of the samples from 300 to 4.2 K that accompanies the short-wave excitation ($\lambda_{ex} = 337{,}1$ nm) results in a decrease of the absolute and relative intensities of the long-wave components of the green-orange emission band. In particular, at $T = 300$ K, the maximum of its envelope lies at $\lambda_m \approx 550$ nm for $KAlP_2O_7(Cr)$ crystals and at $\lambda_m \cong 560$ nm for $KInP_2O_7(Cr)$ samples. With decrease in the temperature up to 4.2 K, the maximum of the envelope of the green-orange band shifts towards the short-wave region and appears at $\lambda_m \approx 510$ and $\lambda_m \approx 550$ nm for $KAlP_2O_7(Cr)$ and $KInP_2O_7(Cr)$ crystals, respectively (Figs. 2,a, 2,b). For aluminum diphosphates at similar variations in the temperature and the excitation wavelength $\lambda_{ex} = 337.1$ nm, a relative intensity of the red luminescence band also increases. Moreover, with increase in the temperature from 4.2 to 77 K, its maximum shifts towards the long-wave side, while it moves with increase in the temperature from 77 to 300 K towards the short-wave side(Fig. 2,a).

Having analyzed the influence of the concentration and temperature on the luminescence spectra of the crystals under investigation, we have every reason to conclude that the band of red luminescence of double aluminum phosphates is due to admixtures: it is a result of vibronic transitions in admixture chromium ions. This fact is confirmed by the results of analyzing the excitation spectra for the red luminescence and the reflectance spectra for $KAlP_2O_7(Cr)$ crystals (Fig. 3). For comparison, Fig. 3 also shows the reflectance spectra for $KInP_2O_7(Cr)$ crystals.

As is obvious, it would be better to compare the luminescence excitation spectra of the samples with their absorption spectra. But, in view of the polycrystalline structure of the samples, we did not succeed in obtaining the high-quality absorption spectra. The reflectance spectra are known to related, to a certain extent, to the peculiarities of absorption characteristics. In the obtained reflectance spectra, the maximum of the envelope of the short-wave band is located at $\lambda_m = 480$ nm. The long-wave band of the reflectance spectrum seems to be complicated, because we can distinguish at least four peculiarities that have a form of two maxima at $\lambda_m = 670$ and 705 nm and two arms in the neighborhood of 630 and 787 nm. Comparing the reflectance spectra of aluminum and indium diphosphate, we note that the spectrum of In is less intense and is shifted towards the short-wave region. In particular, the short-wave band is shifted by 30 nm, while the long-wave one by 50 nm. The reflectance spectrum of the crystal with In also consists of two bands, and the long-wave band, like the case of aluminum crystals, is complicated and includes four weakly manifested peculiarities at the wavelengths $\lambda_m = 590, 640, 665,$ and 700 nm. Similarly to the reflectance spectra, the excitation spectra of the red luminescence of the $KAlP_2O_7(Cr)$ samples are characterized by two wide intense bands in the ranges $540 - 690$ nm ($14500 - 18500$ cm^{-1}) (band I) and $385 - 520$ nm ($19300 - 26000$ cm^{-1}) (band II). In the ultraviolet region of the excitation spectra of the red emission, one can observe one more low-intense band in the range $280 - 350$ nm ($35700 - 28600$ cm^{-1}) (band III) with a principal maximum at $\lambda_m \approx 300$ nm. Most likely, it is not observed in the reflectance spectra due to its relatively low intensity.

The excitation spectra of the red luminescence for $KAlP_2O_7(Cr)$ crystals are similar to the reflectance spectra not only in their general form but also in details of their structure. Indeed, it is easy to note that certain maxima and minima in the excitation spectra correspond to certain extrema of the reflectance spectra (Fig. 3). Moreover, the increase in the temperature of the samples from 4.2 to 300 K does not cause any essential changes in the excitation spectra. The temperature influence manifests itself only in a somewhat change of the ratio

of the intensities of components of the both bands of the spectrum. In particular, at $T = 300$ K, one can observe an increase of the relative intensity of the short-wave components forming the excitation spectra of the red luminescence of $KAlP_2O_7(Cr)$ crystals. Thus, the both types of spectra (reflectance and excitation ones) are of similar origin, since they are conditioned by the interaction of light with admixture chromium ions. One can state that, in $KAlP_2O_7(Cr)$ crystals, the basic transitions accompanied with the excitation of the admixture take place at the wavelengths (frequencies) corresponding to the following maxima λ_m, nm (ν_m, cm^{-1}) in the excitation spectra: band III — 290 (34300) and 300 (33000); band II — 410 (24400), 430 (23260), 443 (22600), 455 (21980), 473 (21000), 505 (19800); band I — 585 (17000), 630(15900), and 650 (15400). In Fig. 3, curve 3, the positions of the mentioned maxima are marked with solid arrows.

Let us discuss, in more details, the behavior of the luminescence spectra of the both crystals depending on the excitation wavelength. As already noted above, for $KAlP_2O_7(Cr)$ crystals, the excitation within excitation bands II and III (the range 208—520 nm) gives rise to the both luminescence bands (the green-orange and the red ones), while, for $KInP_2O_7(Cr)$, there appears only the green-orange band. The excitation within the most long-wave excitation band I (the range 530—680 nm) results in the appearance of the red luminescence band alone (Fig. 4). The form of this band under the conditions of long-wave excitation depends on the temperature of the samples. With decrease in the temperature from 300 to 4.2 K, the band becomes narrower. In addition, there appear humps against the background of its short-wave side in the range 700—725 nm, which can be considered as a manifestation of details of the fine structure. In the case of the excitation by light with $\lambda_{ex} = 632.8$ nm, these details can be observed explicitly as a sharp narrow peak at $\lambda_m = 708$ nm and shoulders with a lower intensity in the neighborhood of 704, 712, and 725 nm. We note that, under such an excitation, the position of the maximum of this band does not vary with temperature contrary to the case of the short-wave excitation (Fig. 4).

4. Discussion of the Results

The presented results demonstrate that both doped und undoped $KAlP_2O_7$ and $KInP_2O_7$ crystals have luminescence properties. That's why, allowing for the foregoing discussion and the obtained experimental data, we can state that the luminescence of doped $KAlP_2O_7(Cr)$ and $KInP_2O_7(Cr)$ crystals is caused by
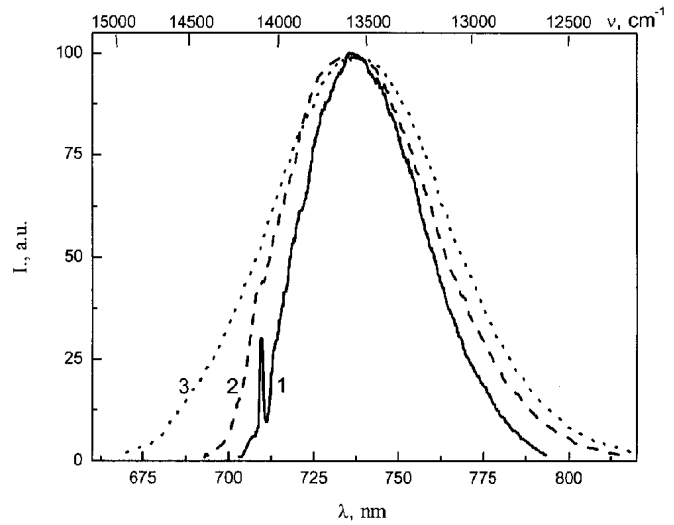

Fig. 4. Luminescence spectra of $KAlP_2O_7(Cr)$ crystals ($C_{Cr} = 0.08$ mass%), $T = 4.2$ (1), 77 (2), and 300 K (3), $\lambda_{ex} = 632.8$ nm

the matrix that generates its intrinsic emission as well as admixture chromium ions that initiate the emission of the luminescence centers formed by them. As a matter of fact, the emission of undoped crystals in the blue-green band can be conditioned by various reasons both those inherent in the matrix itself and those caused by uncontrolled factors. The experimental and literature data available at present are insufficient for discussing the nature of this emission. As for the discussion of the emission associated with chromium admixtures, it requires the data concerning possible variants of the ingress of chromium ions to the lattice of KAl/InP_2O_7 phosphate crystals as well as the spectroscopy of chromium ions in oxide crystals.

The base of the structure of aluminum and indium double phosphate crystals of monoclinic syngony is a three-dimensional skeleton formed by Al/InO_6 octahedra and P_2O_7 diphosphate groups connected by means of common oxygen vertices. Each of the octahedra is connected with five diphosphate groups; moreover, one of them is connected bidentately, while the other four are the bridging ones. Comparing aluminum and indium compounds, one can observe an increase of the interatomic distance in the octahedron (the average distances are $R(Al—O) = 1.89$ and $R(In—O) = 2.12$ Å). Positively charged ions in these compounds are potassium ions with charge +1, aluminum and indium ones with charge +3, and phosphorus ions with charge +5. Following the neutrality principle and taking into account the ratio of the dimensions of the mentioned ions, one can state that chromium arranges in the most optimal way in the form of Cr^{3+} ions

at the positions of aluminum or indium in AlO_6 or InO_6 octahedra, respectively. Indeed, the charges of chromium, aluminum, and indium are the same, 3^+, while their radii amount to 0.073, 0.062, and 0.080 nm, respectively (the ratio of the radii $R(Cr^{3+})/R(Al^+)=$ 1.17 and $R(Cr^{3+})/R(In^+) = 0.91$), which is rather favorable for the above-mentioned substitution of aluminum or indium ions in a KAl/InP_2O_7 lattice by Cr^{3+} ions.

The luminescence of Cr^{3+} ions in the octahedral surrounding in a solid is known to reveal itself in the form of a wide red band and (or) two narrow lines (the so-called R-lines). In the case where the latter manifest themselves, they must lie in the short-wave part of the red luminescence band. The maxima of the mentioned bands and lines are located in the range 670—800 nm, which is determined by the strength of the crystal field Dq, in which Cr^{3+} ion is located [2—8]. It is known that R-lines result from the $^2E \to {}^4A_2$ transition, while the red band is identified as the one corresponding to $^4T_2 \to {}^4A_2$ radiation transitions, where $^4A_2$ is the ground state of a Cr^{3+} ion.

As a matter of fact, Cr^{3+} ions can take positions of other cations of the KAl/InP_2O_7 crystal lattice, namely, those of K^+ and P^{3+} ions. However, this situation is much more complicated than the substitution of Al^{3+}/In^{3+} ions by Cr^{3+} ones due to the essential difference between their radii and charges. The ratios of the radii of Cr^{3+} and potassium ions and Cr^{3+} and phosphorus ones are as follows: $R(Cr^{3+})/R(K^+)= 0.446$ and $R(Cr^{3+})/R(P^{5+})= 3.62$. However, one should not completely discard the possibility of the ingress of Cr^{3+} ions at the positions of K^+. In this case, it is just necessary to provide the compensation of the excess charge 2^+, for example, at the expense of two vacancies of neighboring potassium ions.

It's worth noting that there also exists a fundamental possibility for chromium to take positions of phosphorus ions. But, in this case, chromium should be in another charge state. For example, there exists a large number of natural and synthesized compounds, where chromium is located in the tetrahedral oxygen surrounding and has a charge of 6^+ [10]. In defect-free KAl/InP_2O_7 crystals, tetrahedral groups don't exist in the "pure" form, but P_2O_7 diphosphate groups of this crystal can be considered as those formed by two PO_4 groups having one common oxygen ion. In groups of such a kind, phosphorus ions are surrounded by four oxygen ions. Thus, a part of the O_3—P—O diphosphate group can be considered as a PO_4 tetrahedron deformed with respect to geometry and charge. A ratio of the radii of a Cr^{6+} impurity ion and a phosphorus ion in the group is $R(Cr^{6+})/R(P^{5+})= 1.76$, which is quite acceptable for the realization of the variant, where phosphorus ions are substituted by admixture Cr^{6+} ions. In this case, there appears the necessity to compensate the effective charge $+1$, for example, at the expense of a vacancy of one potassium ion.

Thus, considering the variants of the ingress of chromium ions into the lattice of a KAl/InP_2O_7 crystal, it's worth taking into account the possibility of their ingress in the form of Cr^{3+} ions at the positions of aluminum or indium ions and in the form of Cr^{6+} at the position of phosphorus ions, being a part of diphosphate groups, which results in the formation of an O_3—P—$(O$—Cr—$O_3)$ group. It is obvious that an $(O$—Cr—$O_3)$ group is far, by its electron structure, from an ideal free CrO_4^{2-} tetrahedron. But, on the other hand, as was shown earlier, it is just distorted CrO_4 tetrahedra in the matrices of oxide crystals that represent the sources of photo- and X-ray-luminescence [12—15]. Indeed, let us consider luminescence characteristics and the spectra of its excitation that we obtained for $KAl/InP_2O_7(Cr)$ crystals and the luminescence characteristics of CrO_4^{2-} molecular groups that are present as impurities in various matrices (alkali halide crystals, crystals and glasses of alkaline and alkaline-earth elements [12, 13]) or as the components of the crystals of complex oxides (chromates of alkaline and alkaline-earth elements, etc. [14, 15]). Their comparison demonstrates that the long-wave components of the green-orange luminescence, whose intensity increases with the chromium concentration, can be attributed just to the emission of CrO_4^{2-} groups. According to the same data, chromate groups CrO_4^{2-} can also be a core of complex centers, whose emission is characterized by bands lying in the range 600—800 nm. Complex centers of luminescence are mainly formed in crystals with such defects as oxygen vacancies, positively charged impurities, and F-centers.

With regard for the above-stated ideas about possible forms of the existence of chromium ions in a KAl/InP_2O_7 crystal lattice and possible manifestations of their luminescent properties, the results of experimental investigations of the luminescent properties of pure "undoped" crystals as well as those doped with chromium ions, $KAl/InP_2O_7(Cr)$, can be explained in the following way.

In chromium-doped crystals, the intrinsic emission of the matrix itself that lies in the blue-green region of the visible spectrum is supplemented with the green-orange emission of distorted CrO_4^{2-} molecular groups.

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The luminescence of complex centers formed on the basis of the same groups can also cause manifestations of the luminescence of doped crystals in the red spectral region. But taking into account the facts that, first, the form of this band differs from those observed for complex CrO_4^{2-}-centers, secondly, the probability of the formation of such centers is low as compared to that of their formation on the basis of Cr^{3+} ions, and, thirdly, the lines that can be identified as R-lines of the luminescence of Cr^{3+} ions are manifested, one can conclude that the band of the red luminescence of $KAlP_2O_7(Cr)$ crystals is mainly conditioned by radiation transitions in Cr^{3+} ions [especially at low temperatures (4.2—77 K)]. This conclusion concerning the absence of a noticeable contribution of the emission of complex chromate centers based on CrO_4^{2-} groups is confirmed by the absence of luminescence in the region 600—800 nm for $KInP_2O_7(Cr)$ crystals (Figs. 1, 2). A predominant contribution of the emission of Cr^{3+} ions in the region of red luminescence agrees with the similarity of the structure of excitation spectra of this photoluminescence (PL) to the structure that was observed in the spectra of a number of other matrices doped with Cr^{3+} ions. As is known, this structure results from the transitions from the ground state to the numerous levels of excited electron states of Cr^{3+} ions in the crystal field of the matrix [3, 7, 9].

As for the absence of the red PL of Cr^{3+} ions in the luminescence spectra of $KInP_2O_7(Cr)$ crystals, it's worth noting the following. The energies of electron transitions and the positions of the corresponding bands in the absorption and luminescence spectra for Cr^{3+} ions are calculated within the frames of the crystal field theory, where they are determined by the parameter of the crystal field Dq:

$$Dq = \mathrm{const}\frac{q}{R^5}\langle r^4\rangle,$$

where q denotes the charge of a ligand (in our case, O^{2-} ion), R is the distance "impurity ion — ligand", and $\langle r^4 \rangle$ is the average radius of the 3d-orbital of Cr^{3+} ions. It is known that the energy of the $^4T_2 \rightarrow \, ^4A_2$, $\Delta E(^4T_2, \, ^4A_2)$ transition that causes the wide band of the red luminescence is directly proportional to the parameter Dq [16]. Thus, knowing the energy of the given transition for Cr^{3+} ions in $KAlP_2O_7(Cr)$ crystals (from the luminescence spectrum) as well as the distances $R(Al—O)$ and $R(In—O)$, one can estimate the quantity $\Delta E(^4T_2, \, ^4A_2)$ for Cr^{3+} ions in $KInP_2O_7(Cr)$ crystals. Considering that ΔE corresponds to the maximum of the PL band, one can find the quantity $\frac{\Delta E_{Al}}{\Delta E_{In}}$ and

obtain a probable position of the luminescence band that corresponds to the $^4T_2 \rightarrow \, ^4 A_2$ transition for Cr^{3+} in $KInP_2O_7(Cr)$ crystals. Thus,

$$\frac{\Delta_{Al}}{\Delta_{In}} = \frac{Dq_{Al}}{Dq_{In}} = \frac{R_{In}^5}{R_{Al}^5} = \frac{(2.12)^5}{(1.89)^5} = 1.776.$$

The maximum of the red luminescence band of $KAlP_2O_7(Cr)$ crystals, which is associated with the transition $^4T_2 \rightarrow \, ^4 A_2$, lies at $\lambda_{max} = 735$ nm. That's why the maximum of the corresponding band for $KInP_2O_7(Cr)$ crystals must be located at $\lambda_{max} = 1300$ nm. With regard for the possible width of the spectrum of red PL ($\approx 100 \div 150$ nm), it is clear that, in the range of wavelengths lower than 800 nm, we cannot observe this luminescence.

The ideas of the superposition of the luminescence spectra (the intrinsic emission of the matrix, the emission of Cr^{3+} impurity ions, and the emission of the centers based on CrO_4^{2-} molecular groups) allow one to explain the variations that take place in the luminescence spectra depending on the excitation wavelength and temperature. It is obvious that these variations in the form, relative intensity, and positions of the maxima of the green-orange and red bands (Fig. 2) are associated with a change of the contribution of various centers to the summary spectra depending on the excitation wavelength and temperature (Figs. 2, 4). The short-wave excitation (within band III of the excitation spectra) of $KAlP_2O_7$ crystals (in particular, at $\lambda_{ex} = 337.1$ nm) causes the intrinsic emission of the matrix and the emission of distorted CrO_4^{2-} groups. They give rise to the blue-green-orange luminescence band consisting of a number of components (Figs. 1, 2). The light from the range of excitation band II excites the intrinsic luminescence of the matrix less effectively. Therefore, the contribution of bands of the impurity luminescence increases at such an excitation, which is conditioned by the emission of distorted CrO_4^{2-} groups, complex centers based on them, and Cr^{3+} ions (Fig. 2,c).

The temperature variations observed in the spectra at short-wave (Figs. 2,a, 2,b) and long-wave (Fig. 4) excitations are of different nature. Under the short-wave excitation (in particular, at $\lambda_{ex} = 337.1$ nm), a rise in temperature initiates the processes of transfer of the excitation energy from the matrix to CrO_4^{2-} molecular groups and Cr^{3+} ions, which results in an increase of the relative intensity of long-wave components of the green-orange band and the intensity of the red band (Fig. 2,a). These changes are especially noticeable at room temperature (Figs. 2,a, 2,b, curves 3). The possibility

of such a transfer of excitation energy is conditioned by the noticeable overlapping of the absorption (excitation) band of the orange-red impurity luminescence and the band of the intrinsic radiation of the matrix in the range 400—500 nm (Fig. 2,a, curves 1, 4). In this case, a short-wave displacement of the red luminescence band observed at the increase of temperature from 77 to 300 K can result from the increase of the contribution of complex centers based on CrO_4^{2-} groups to the luminescence in the red region. This conclusion is proved by the absence of such a displacement under the highest long-wave excitation within band I (in particular, at $\lambda_{ex} = 632.8$ nm), at which only Cr^{3+} impurity ions are excited. Variations in the form and width of the red luminescence band at $\lambda_{ex} = 632.8$ nm are partly explained by the temperature dependence of the vibronic interaction at the $^4T_2 \to {}^4A_2$ electron transition that gives rise to the red luminescence band. With decrease in temperature, the vibronic interaction subsides, which results in the band narrowing. In addition, a reduction in temperature causes the essential increase in the ^2E level population, whereas that of $^4T_2$ level decreases. As a result, the mentioned factors cause the manifestation of details of the spectra which were hidden at high temperatures in the neighborhood of the red band, in particular, the manifestation of narrow R-lines of the $^2E \to {}^4A_2$ transitions.

5. Conclusions

The luminescence of $KAlP_2O_7$ and $KInP_2O_7$ crystals doped with chromium ions is conditioned by the intrinsic emission of the matrix and the emission of centers formed by chromium ions.

The green-orange luminescence band (the range 450—700 nm) represents a superposition of the intrinsic luminescence of the matrix and the emission of CrO_4^{2-} molecular groups.

The red luminescence band of $KAlP_2O_7(Cr)$ crystals and narrow peaks on its short-wave edge are mainly caused by Cr^{3+} impurity ions that replace Al^{3+} ions of the lattice and are arranged in the octahedral oxygen surrounding.

A similar band of the luminescence of Cr^{3+} ions in $KInP_2O_7(Cr)$ crystals must lie in the infrared spectral region with a maximum at 1300 nm. This statement requires a further experimental verification.

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ЛЮМІНЕСЦЕНТНА СПЕКТРОСКОПІЯ КРИСТАЛІВ ПОДВІЙНИХ ФОСФАТІВ KMP_2O_7 (M = Al, In), ЛЕГОВАНИХ ІОНАМИ ХРОМУ

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Р е з ю м е

Розглянуто люмінесцентні властивості кристалів KMP_2O_7 (M = Al, In) активованих іонами хрому. Спектри люмінесценції цих кристалів складаються з двох основних смуг, які належать в зелено-оранжевій та червоній областям спектра. Положення смуг і їхня форма залежать від типу металу (Al чи In), температури кристала, концентрації домішки і довжини хвилі збуджуючого випромінювання. Складна структура зелено-оранжевої смуги є наслідком суперпозиції випромінювання кристалічної матриці і домішкових іонів хрому в зарядовому стані 6^+, що входять до складу молекулярних груп CrO_4^{2-}. Червона смуга люмінесценції зумовлена випромінювальними переходами в іонах Cr^{3+} в октаедричному кисневому оточенні. Розглянуто вплив сили кристалічного поля на положення червоної смуги люмінесценції. Обговорено можливості входження іонів хрому в різні позиції решітки кристала.