Optical and spectral characteristics of chromium ion doped double alkali-aluminum phosphates

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Diffuse reflection, luminescence, and luminescence excitation spectra of double alkali-aluminum phosphate $MAlP_2O_7$ (M = Na, K, Cs) crystals doped with chromium ion have been considered. The reflection spectrum bands have been ascribed to excitation of Cr^{3+} ion in the crystal lattice. The luminescence spectra include two main bands lying in the green-orange and red spectral regions, respectively. Influence of the alkali metal cation on the "red" luminescence band position has been considered. The complex structure of the "green-orange" band has been shown to be due to superposition of the matrix intrinsic emission and extrinsic emission of chromium ions included in CrO_4^{2-} groups. The "red" luminescence band is caused by radiative transitions in Cr^{3+} ions being in octahedral oxygen environment. Influence of the crystal field, alkali cation type, and the crystal structure type on its spectral characteristics has been discussed.

Проведен анализ спектров диффузного отражения, характеристик люминесценции и ее возбуждения кристаллов двойных фосфатов щелочного металла и алюминия ряда $MAlP_2O_7$ (M = Na, K, Cs) легированных ионами хрома. Полосы в спектрах отражения обусловлены возбуждением ионов хрома Cr^{3+} в решетке кристалла. Спектры люминесценции состоят из двух основных полос, которые расположены в зелено-оранжевой и красной областях спектра, соответственно. Рассмотрено влияние типа катиона щелочного металла на положение "красной" полосы люминесценции. Показано, что сложная структура "зелено-оранжевой" полосы люминесценции обусловлена суперпозицией собственного свечения матрицы кристалла и примесных ионов хрома, которые входят в состав группы CrO_4^{2-}. "Красная" полоса люминесценции обусловлена излучательными переходами в ионах Cr^{3+} в октаэдрическом кислородном окружении. Рассматривается влияние кристаллического поля, типа катионов щелочного металла и структурного типа кристалла на его спектральные характеристики.

Recently, an increasing interest is observed in investigation of spectral properties of double phosphates doped with transition and rare-earth metal ions. This is due to the possible use thereof as laser materials generating in a wide spectral range as well as materials for ionizing radiation sensors. Chromium ions are among most popular activators. Those are used as generating ions in laser crystals, effective sensitizers of trivalent rare-earth ion luminescence, etc. [1, 2]. The use of chromium ions in various sensors is known as well [3]. Numerous works are aimed at study of energy transfer and redistribution processes in a doped crystal matrix under interaction with exciting radiation. A great attention is given also to formation of various luminescence center types in various nearest neighborhoods. Unfortunately, the influence of the crystal
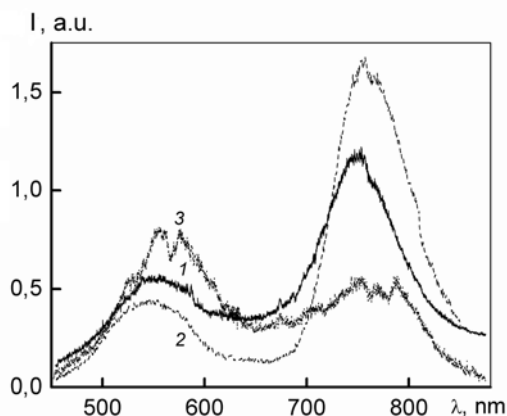
Fig. 1. Luminescence spectra of $MAlP_2O_7(Cr)$ crystals: M = Na (*1*), K (*2*). C_{Cr} = 0.02 mass %, λ_{ex} = 337.1 nm.

structure type on the above-mentioned processes remains still scarcely elucidated in literature. In this connection, this work is aimed at consideration of spectral properties of chromium doped double pyrophosphates $MAlP_2O_7$ (M = Na, K, Cs) where the structure depends on the alkali metal cation. Indeed, the $MAlP_2O_7(Cr)$ compounds are not isotypic (although belonging to one and the same monoclinic system of the $P2_1/c$ space group), but are crystallized in various structure types. The Na containing crystals exhibit one type while those with K and Cs, another. The oxygen coordination of the alkali metal cation is different (10 for M = K, Cs but 8 for M = Na) as well as the arrangement thereof in the channel cavities of the 3D frameworks and the number and shape of the formed cavities [4, 5]. That is why just the above-mentioned compounds $MAlP_2O_7$ (M = Na → K → Cs) were used as the materials for doping with chromium ions.

The polycrystalline samples of $MAlP_2O_7$ (M = Na, K, Cs) were synthesized from melted mixtures of M_2O–Al_2O_3–P_2O_5 oxides, all the materials were of chemical purity grade. The activator ions were introduced by adding Cr_2O_3 to the mixture, the chromium concentration in the raw mixture was 0.02 or 0.08 % by mass. The luminescence was studies at 4.2, 77, and 300 K using a liquid helium or liquid nitrogen cryostat, respectively, in the first two cases. The luminescence was excited using a ILGI-501 (λ_{ex} = 337.1 nm) or LG-22 (λ_{ex} = 632.8 nm) laser. The luminescence excitation spectra were studied using a

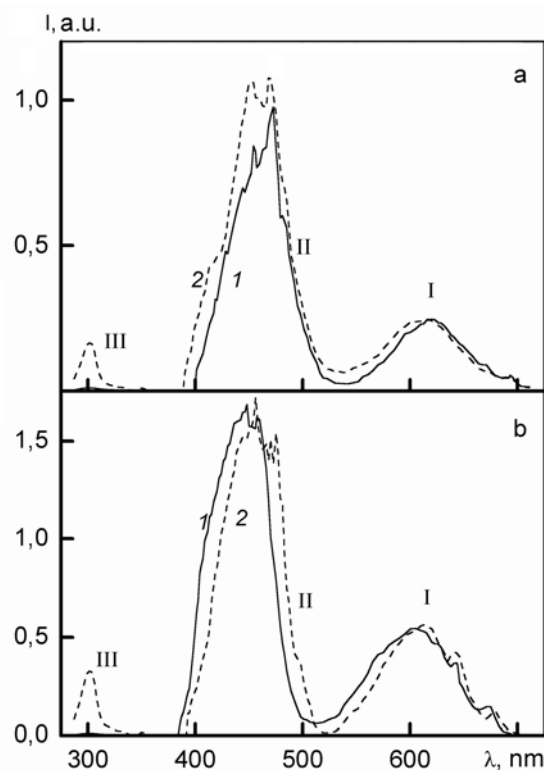Fig. 2. Luminescence excitation spectra of $MAlP_2O_7(Cr)$ crystals: M = Na (*1*), K (*2*). C_{Cr} = 0.02 % (mass), λ_{ex} = 740 nm. T = 300 K (a), 77 K (b).

DXeE1-1000 xenon lamp (the exciting wavelength region 300 to 650 nm). The emission was extended into spectrum by a DMR-4 double prism monochromator. A DFS-12 spectrometer (reciprocal linear dispersion 10 Å/mm) was used to record the luminescence and luminescence excitation spectra. The differential reflection spectra (for chromium doped samples against undoped ones) were taken using a SPECORD M40 spectrometer.

Under excitation from the 300–650 nm exciting wavelength region λ_{ex} (33000–14500 cm^{-1} excitation frequencies), the chromium doped aluminum double pyrophosphates show an intense luminescence within essentially entire visible light region. The emission spectra comprise two bands: a short-wavelength one ("green-or-ange") in the 350–650 nm range with the envelope maximum (λ_m) about 550 nm at the sample temperature from 4.2 to 300 K, and a longer-wavelength ("red") band in the 700–850 nm range with λ_m at 730–750 nm. The position and structure of those bands depend on the dopant concentration, the sample temperature, the exciting wavelength and
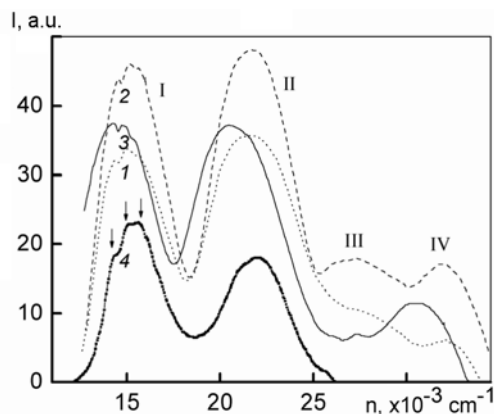
Fig. 3. Diffuse reflection spectra of $MCrP_2O_7$ crystals: M = Na (*1*), K (*2*), Cs (*3*) and $KAlP_2O_7(Cr)$ crystal (C_{Cr} = 0.08 mass %). T = 300 K.

Fig. 4. Luminescence spectra of $MAlP_2O_7(Cr)$ crystals: M = Na (*1*), K (*2*), Cs (*3*). C_{Cr} = 0.08 mass %, T = 300 K, λ_{ex} = 632.8 nm.

the alkali metal cation (Figs. 1, 4, 5). Let the alkali metal cation influence in the Na → K → Cs sequence on the spectral and luminescence properties of the $MAlP_2O_7(Cr)$ be considered in more detail. The short-wavelength luminescence band asymmetry and the presence of inflections and maxima therein (Fig. 1) evidences its complex character. It consists no doubt of several weakly distinguishable components. Any effect of the alkali metal component on the band structure is not observed. In contrast, as to the red luminescence band, its maximum is shifted towards longer wavelengths in the Na → K → Cs sequence (see Fig. 1). In the excitation spectra of that band, two broad bands are present lying in the 550–700 nm (18180–14300 cm^{-1}, Band I) and 380–525 nm (26300–19000 cm^{-1}, Band II) as well as a low intensity band in the UV region at 280–350 nm (35700–28600 cm^{-1}, Band III) (see Fig. 2). The Bands I and II are seen to be complex, 3 to 5 components can be distinguished therein for each sample. The whole excitation spectrum for $KAlP_2O_7(Cr)$ crystals is seen to shift a little towards longer wavelengths as the temperature drops down to 77 K. The temperature lowering can be noted to result in increased relative intensity of the Band II for Na-containing crystals and in enhanced separation of the Band I components for all the samples.

Besides of the luminescence properties of $MAlP_2O_7$ (M = Na, K, Cs) crystals, the reflection spectra thereof were studied. Fig. 3 presents the reflection spectra of crystal matrices for double chromium pyrophosphates $MCrP_2O_7$ (M = Na, K, Cs) and
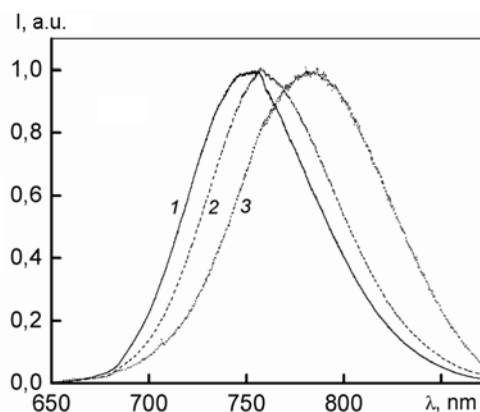
$KAlP_2O_7(Cr)$ crystals. In the reflection spectra of $MCrP_2O_7$, four (at M = Na, K) or three (at M = Cs) bands are observed in the following spectral regions: 12500–18500 (I), 18500–25500 (II), 25500–30000 (III), and 30500–34500 (IV) cm^{-1} (at M = Na, K) and 11500–17500 (I), 17500–26000 (II), and 28000–33300 (III) cm^{-1} (at M = Cs). For $KCrP_2O_7$ crystals, the intensity of the all four bands is higher, and the III and IV bands are better separated. The relative intensity of the IV band is increased when passing from Na to Cs. In the reflection spectra of $MAlP_2O_7(Cr)$ crystals, only the bands I and II have been studied lying in the same spectral region as the corresponding bands for $MCrP_2O_7$ phosphates. For all the samples, the I band is seen to be complex and at least three components can be distinguished therein. The maxima positions for those components remains essentially unchanged when passing from Na to Cs. For $KAlP_2O_7(Cr)$ double phosphate, the values thereof (shown by arrows in Fig. 3) are about 15870 (630), 14925 (670) and 14180 (705) cm^{-1} (nm). Thus, when comparing the reflection spectra and the luminescence excitation ones, it is to note the general similarity thereof as well a certain similarity in details such as the Band I structure, etc. (cf. Figs. 2 and 3).

Let the "red" luminescence band behavior be considered in more detail as the alkali cation chances in the Na → K → Cs sequence. The long-wavelength excitation within limits of the Band I of the luminescence excitation spectra initiates the broad "red" luminescence band. The band maximum is shifted towards longer wavelengths
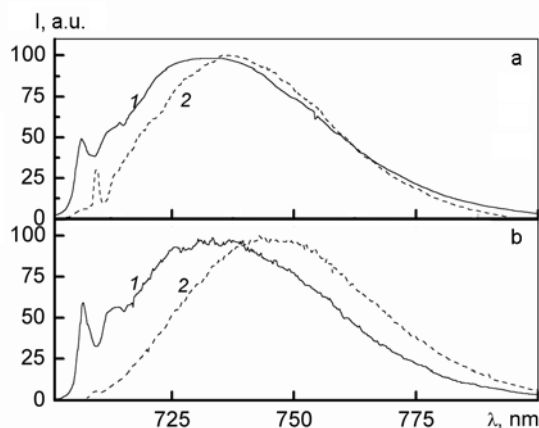
Fig. 5. Luminescence spectra of $MAlP_2O_7(Cr)$ crystals: M = Na (1), K (2). C_{Cr} = 0.02 mass %, λ_{ex} = 623.8 nm. T = 4.2 K. C_{Cr} = 0.02 mass % (a), 0.08 mass % (b).

by about 10 nm when passing from Na to K and by about 20 nm when passing from K to Cs (Fig. 4). Another feature of the "red" luminescence band consists in a thin structure shaped as a narrow peak and a shoulder that is observable as the temperature is 4.2 K. The position of those components depends on the alkali metal cation, being shifted towards longer wavelengths by about 2 nm when passing from Na to K. So, the narrow peak is at about 607 and 609 nm for $NaAlP_2O_7(Cr)$ and $KAlP_2O_7(Cr)$ crystals, respectively. As to the shoulder, it is better observable for $NaAlP_2O_7(Cr)$ crystals and less visible for $KAlP_2O_7(Cr)$ ones (Fig. 5).

The results obtained show that the luminescence of chromium-doped $MAlP_2O_7$ (M = Na, K, Cs) crystals is similar in characteristics for all the crystals. For example, the two bands ("geen-orange" and "red" ones) in $CsAlP_2O_7(Cr)$ crystal luminescence spectra are similar in position and structure to the corresponding bands in luminescence spectra of for $NaAlP_2O_7(Cr)$ and $KAlP_2O_7(Cr)$ ones [6, 7]. Since the changes in $CsAlP_2O_7(Cr)$ crystal luminescence spectra caused by variation of temperature, excitation wavelength, and chromium ion concentration are similar to the corresponding changes observed for Na and K containing crystals, the emission nature for all three studied crystal types is no doubt the same. Thus, the luminescence is due to the crystal matrix that generates intrinsic emission as well as to chromium impurity ions inducing the emission of luminescence centers including those ions. The "blue-green" emission of the matrix may be due to various factors,

both inherent in the matrix itself and caused by uncontrollable effects. The experimental results and literature data available to date are insufficient for discussion on that emission. To consider the emission of extrinsic chromate centers, data are necessary on possible variants of chromium ion entry to pyrophosphate crystal lattice and chromium ion spectral properties in oxide crystals.

Luminescence of octahedrally coordinated chromium ion Cr^{3+} in solids is known to appear as a broad red band and/or as two narrow so-called R-lines. The latter, if present, should be positioned at the short-wavelength side of the "red" emission band. The bands and lines mentioned have maxima in the 670–800 nm range that is defined by the strength of crystal field Dq containing the Cr^{3+} ion [2, 8–10]. The R-lines are known to be caused by the $^2E \rightarrow {^4A_2}$ transition while the "red" band is identified to correspond to radiative transitions $^4T_2 \rightarrow {^4A_2}$ where $^4A_2$ is the ground state of Cr^{3+} ion.

In principle, Cr^{3+} ions may also occupy the positions of other cations in the $MAlP_2O_7$ crystal lattice, namely, those of M ions (M = Na, K, Cs) as well as of P^{3+}. However, in those cases, the situation is much more complex than at substitution Cr^{3+} for Al^{3+} due to inconsistency in ionic radii and charges. The radius ratios of Cr^{3+} ion to alkali metal and phosphorus ones are as follows: $R(Cr^{3+})/R(Na^+)$ = 0.653; $R(Cr^{3+})/R(K^+)$ = 0.446; $R(Cr^{3+})/R(Cs^+)$ = 0.371; $R(Cr^{3+})/R(P^{5+})$ = 3.62. Nevertheless, the possibility of Cr^{3+} ion substitution for alkali metals cannot be excluded completely. In this case, only the excess charge 2+ must be compensated, for example, at the expense of two vacancies of neighboring alkali metal ions. It is to note also that chromium may occupy in principle the phosphorus ion site, but in this case, chromium must be in another charge state. Numerous natural and synthetic compounds are known where chromium is in tetrahedral oxygen environment and bears +6 charge [11]. In defect-free $MAlP_2O_7$ crystals, the are no "pure" tetrahedral groups; however, diphosphate groups P_2O_7 in that crystal can be considered to be formed by two PO_4 groups having one common oxygen ion. In such groups, phosphorus ions are surrounded by four oxygen ions. Thus, the part O_3–P–O of the diphosphate group can be considered as a PO_4 tetrahedron distorted in geometry and charge. In this case, the ratio $R(Cr^{6+})/R(P^{5+})$ = 1.76 and is

relatively acceptable for Cr^{6+} substitution for phosphorus ion. This variant requires compensation of effective charge +1, for example, at the expense of one alkali ion vacancy.

Thus, when considering the variants of chromium ion entering to the $MAlP_2O_7$ crystal lattice, both the Cr^{3+} ion substitution for aluminum ion and Cr^{6+} ion substitution for phosphorus ion in diphosphate croup with formation of a O_3–P–(O–Cr–O_3). The (O–Cr–O_3) group electron structure is of course far from that of the ideal $CrO_4{}^{2-}$ tetrahedron. On the other hand, however, it is just distorted CrO_4 tetrahedrons in oxide crystal matrices have been shown to be the source of photo- and X-ray luminescence [12–15]. In fact, when comparing the luminescence characteristics and excitation spectra obtained in this work for $MAlP_2O_7(Cr)$ crystals with those of molecular $CrO_4{}^{2-}$ groups present as impurities in various matrices (alkali halide crystals, alkali and alkali-earth halide crystals and glasses [12, 13]) or as components of complex oxide crystals (alkali and alkali-earth chromates, etc. [14, 15]), it is seen that the long-wavelength components of the "green-orange" luminescence can be ascribed just to $CrO_4{}^{2-}$ groups. Moreover, the $CrO_4{}^{2-}$ group may be also the core of complex centers emitting in the 600–800 nm range. The complex emission centers are formed mainly in crystals containing defects (oxygen vacancies, positively charged impurities, and *F*-centers). Thus, in chromium-doped crystals, the intrinsic "blue-green" emission of the matrix is supplemented by the "green-orange" emission of distorted molecular $CrO_4{}^{2-}$ groups. The emission of complex centers including those groups may be responsible also for the "red" luminescence of the doped crystals. However, taking into account that (i) that band differs in the shape from those observed for complex $CrO_4{}^{2-}$ centers, (ii) the formation probability of such centers is rather low as compared to that of centers including Cr^{3+} ions, and (iii) the presence of lines that can be identified as the *R*-lines of Cr^{3+} ion luminescence, the "red" luminescence band of $MAlP_2O_7(Cr)$ crystals is due mainly (in particular, at low temperatures such as 4.2 and 77 K) to radiative transitions in Cr^{3+} ions.

The concepts of superposition in luminescence spectra (the intrinsic matrix emission + emission of impurity Cr^{3+} ions + emission of centers including molecular $CrO_4{}^{2-}$ groups) make it possible to explain the changes taking place in the luminescence spectra depending on the alkali metal cation and the dopant concentration. Those changes in the shape, relative intensity, and maximum position of the "green-orange" and "red" bands (Figs. 1, 4, 5) seem to be due to changing contributions of specific centers to the resulting spectra, depending on the cation type in the crystal and on the amount of chromium ions involved in formation of the emission centers. The short-wavelength excitation of $MAlP_2O_7(Cr)$ crystals within limits of the Band III of excitation spectra (in particular, at $\lambda_{ex} = 337.1$ nm) gives rise to the intrinsic matrix emission and emission of distorted $CrO_4{}^{2-}$ groups that results in formation of the "blue-green-orange" luminescence band consisting of several components (Fig. 1).

Changes in the red luminescence band shape and width (Figs. 4, 5) at $\lambda_{ex} = 632.8$ nm are explainable in part by temperature dependence of electron vibration interaction at the $^4T_2 \rightarrow {}^4A_2$ transition responsible for the "red" band. As the temperature drops, the electron vibration interaction becomes weakened, thus causing the band narrowing. Moreover, the occupancy of the ^2E level increases considerably as the temperature decreases while that of the $^4T_2$ one drops. These factors result in appearance of the spectrum details that are concealed at high temperatures, in particular, of the narrow *R*-lines of $^2E \rightarrow {}^4A_2$ transition.

The red shift of the "red" luminescence band maximum at the passage from Na to Cs as well as the similar shift in the "red" luminescence excitation spectra at low temperatures is explained as follows. It is known that the electron transition energies and the positions of corresponding bands in the reflection and luminescence spectra are calculated for Cr^{3+} ions within the crystal field theory where those are defined by the crystal field parameter Dq and the Rack parameter B. The ionic radius increase in the Na $\rightarrow$ K $\rightarrow$ Cs sequence (0.095, 0.133, and 0.167 nm, respectively) seems to result in reduction of the Dq/B value that, in turn, according to the Tanabe-Sugano diagram, must cause a reduction of the $^4T_2 \rightarrow {}^4A_2$ transition energy that defines the "red" luminescence band, that is, its red shift.

To conclude, the luminescence of $MAlP_2O_7$ crystals (M = Na, K, Cs) doped with chromium ions is a superposition of the intrinsic matrix emission and emission of centers including chromium ions. The "green-

orange" luminescence (450–650 nm range) is due to the intrinsic matrix emission (short-wavelength components) and the emission of molecular CrO_4^{2-} groups that are responsible mainly for the long-wavelength components of that band. The "red" luminescence band of $MAlP_2O_7(Cr)$ crystals and narrow peaks at its short-wavelength wing are caused mainly by Cr^{3+} impurity ions that substitute the lattice Al^{3+} ions and are in octahedral oxygen environment. The influence of alkali metal cations in the $Na \rightarrow K \rightarrow Cs$ sequence overcomes the effect of the crystal structure type change on the spectral and luminescence properties of $MAlP_2O_7$ crystals.

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Оптичні та спектроскопічні характеристики подвійних фосфатів лужних металів та алюмінію, легованих іонами хрому

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Проведено аналіз спектрів дифузного відбивання, характеристик люмінесценції та її збудження кристалів подвійних фосфатів лужного металу та алюмінію ряду $MAlP_2O_7$ (M = Na, K, Cs) легованих іонами хрому. Смуги у спектрах відбивання пояснюються як такі, що зумовлені збудженням іонів хрому Cr^{3+} у гратці кристала. Спектри люмінесценції складаються з двох основних смуг, які знаходяться у зелено-оранжевій та червоній областях спектру відповідно. Розглянуто вплив типу катіона лужного металу на положення "червоної" смуги люмінесценції. Показано, що складна структура "зелено-оранжевої" смуги люмінесценції зумовлена суперпозицією власного свічення матриці кристала та домішкових іонів хрому, що входять до складу групи CrO_4^{2-}. "Червону" смугу люмінесценції зумовлено випромінювальними переходами в іонах Cr^{3+} в октаедричному кисневому оточенні. Розглядається вплив кристалічного поля, типу катіонів лужного металу та структурного типу кристала на його спектральні характеристики.