THE LUMINESCENCE PROPERTIES *Zn/Mn* PYROPHOSPHATE

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One diphosphate zinc, manganese and magnesium are known for their practical application. On this basis, produce heat-resistant pigments, catalysts, solid electrolytes, fluids and anticorrosion t. E. Are known and their optical properties. Diphosphate, which have a membership of both zinc and manganese (magnesium) content that can be controlled to change, are compared with individual diphosphate others for specific objectives - improving the physical, chemical, and therefore performance. Obviously, they Optical particular luminescent properties are also different from the characteristics of individual diphosphate.

The purpose of research - to explore the luminescent properties of anhydrous double phosphates of divalent metal zinc / manganese

Materials and methods of research. Elucidation of the synthesis conditions specified diphosphate concentration series were performed using the method of final concentrations. As the initial reagents used in aqueous solutions of sulphate ZnSO4 • 7H2O, MnSO4 • 5H2O and diphosphate K4P2O7 mark "ch.d.a." How were taken following the best ratio in the reactants: P2O74 - / (Zn2 + + Mn2 +) = 0,2; k = Zn / Mn changed within 5,67-0,8. Anhydrous crystals by heating got synthesized pentahydrate to a temperature T = 853 K.

Luminescence studied at T = 4,2, 77 and 300 K. The samples were placed in a helium or nitrogen cryostat, helium or liquid nitrogen at a temperature of 77 samples or 4.2 K respectively. Luminescence excited by laser radiation YLHY-501 (excitation wavelength = 337.1 nm -1000) and xenon lam (excitation wavelength range 300 - 650 nm), which laid out a range with a double prism monohroma¬tora DCC - 4. The spectrometer DFS - 12 (inverse linear dispersion 10 Å / mm) was used to record spectra of luminescence.

Luminescence spectra under excitation in the vacuum ultraviolet excitation and spectra in this field measured at the station SUPERLUMI DESY synchrotron in. Hamburg (Germany). Luminescence spectra were recorded in the wavelength range 275 - 950 nm and excitation spectra of luminescence - in the range of 50 - 334 nm at temperatures ranging from low (helium) 10 K to 300 K.

X-ray spectra were registered while continuous X-ray irradiation source within about 1,200 s at room temperature and at the temperature of liquid nitrogen (T = 300 K and 77 respectively).

Results. Fluorescent properties of crystals diphosphate divalent metal Zn2-hMnhP2O7 studied in a wide wavelength range of excitation, λzb = 50 - 630 nm, and at temperatures from 4.2 to 300 K. In the spectra of photoluminescence (PL) of individual zinc diphosphate, Zn2P2O7, at T = 300 K there is broad complex band blue - pink envelope with maximum radiation in the vicinity of 475 nm (Fig. 1, curve 1).

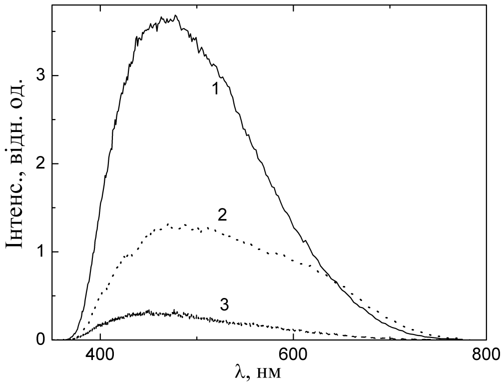

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Fig. 1. PL spectra Zn2P2O7 (1), Zn1,04Mn0,96P2O7 (2), Mn2P2O7 (3), T = 300 K, λzb = 337.1 nm

With the manganese compound consisting PL intensity decreases more than 2 times. This increases the relative intensity of the PL wavelength side of the spectrum in the 500 - 600 nm and in the range 600 - 750 nm, there is a subtle component spectrum (Fig. 1, curve 2). With further increase the content of Mn (x> 1) the intensity of the wavelength of the PL spectrum falls and compound Mn2P2O7 spectrum has a maximum at 450 - 470 nm (Fig. 1, curve 3).

Relegation from room temperature samples to 77 K the distinct (~ 6 times) decline in short-described PL intensity, but at the same time in the field of long-wave radiation appears intense red emission band with a maximum, in the vicinity of 690 nm (Fig. 2).

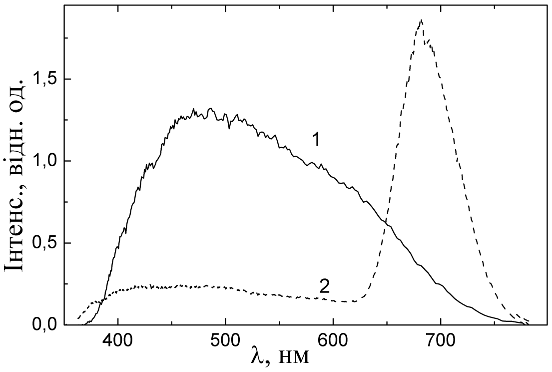

Fig. 2. PL spectra of crystals Zn1,04Mn0,96P2O7. T = 300 (1) and 77 K (2) λzb = 337.1 nm

A line of red emission spectra of radiation prevails in phosphate Zn1,04Mn0,96P2O7 not only of the latter. In the X-ray spectra (RL) at low temperatures prevailing intensity of the color intensity shortwave band at ~ 100 times, and at room temperature this band as of the latter - absent (Fig. 3). Excitation rigid vacuum ultraviolet it dominates the luminescence throughout the temperature range 4.2 - 300 K (Fig. 3).

The intensity of the X-ray and (RL), since the exposure of the samples X-rays versus slightly depending on the type of compound, if samples irradiated at T = 77 K (Fig. 4, curves 2, 3, 5), and pretty much varies depending on the composition of compound if the sample is irradiated at room temperature (Fig. 4, curves 1, 4).

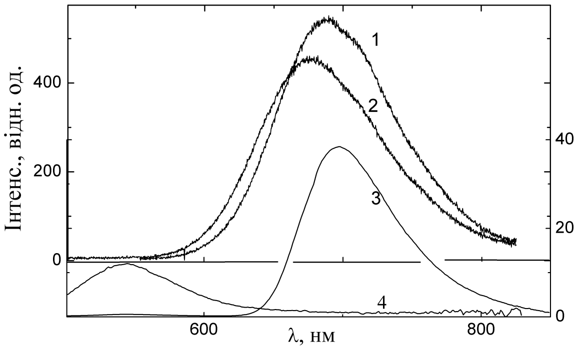

Fig. 3. luminescence spectra under UV excitation (1, 2; RL spectra (3, 4) compounds Zn1,04Mn0,96P2O7; T = 10 (1) and 300 (2) and 77 (3) and 300 K (4) □sb

At room temperature, dose dependent and (RL) is much stronger in the case of individual zinc phosphate (curve 1) than in the case of double phosphate Zn1,04Mn0,96P2O7 (Fig. 4, curve 4).

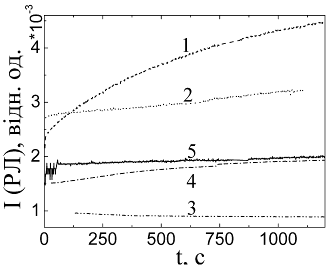

Fig. 4. Crooked I (RPL) for compounds Zn2P2O7 (1, 2), Zn1,04Mn0,96P2O7 (3, 4) and Mn2P2O7 (5) depending on the exposure time, T = 300 (1, 4) and 77 K (2 3, 5)

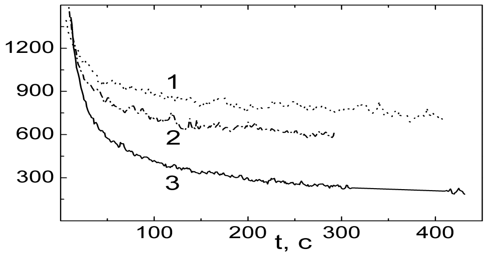

Fig. 5. Curves phosphorescence compounds Zn2P2O7 (1, 2), Zn1,04Mn0,96P2O7 (3); T = 300 (1) and 77 C (2, 3)

These traits. 4 correlated with data on the effect of temperature on the rate of attenuation of phosphorescence, the temperature decreases from room Zn2P2O7 samples to 77 K phosphorescence attenuation is faster (Fig. 5, curves 1, 2). Replacing zinc manganese atoms also leads to more rapid attenuation of luminescence (Fig. 5).

These data indicate that traps are responsible for storing svitlosumy as in undoped and doped in Magnesium compounds are relatively shallow, lower the temperature to 77 K has strongly reduces the likelihood of release of these media. In addition, these data suggest that manganese ions create new levels of delight, and effectively interact with traps and part of electrons filled with traps release the over, blocking, thereby switching to channel their own centers of radiation matrix.

Research results curves thermally luminescence (TSL) are consistent with the above data on the behavior of storing curve svitlosumy, phosphorescence attenuation curves, RL spectra and luminescence spectra when excited by vacuum ultraviolet light. Indeed, if the individual phosphate Zn2P2O7 observed two distinct peaks at 140 and 184 K in the low part of the curve TSL and two low intensity peaks in the high temperatures at 265 and 295 K, then the solid solution range Zn1,04Mn0,96P2O7 traps are similar, but mostly nonuniform expanded: TSL observed in the spectrum of a broad band, which is in the same temperature range 100 - 250 K, and therefore it can be regarded as formed by the superposition of the peaks above, provided their energy heterogeneity. In addition to the double phosphate are added and some new peaks. This is obviously the peak in the low, ~ 120 K, and particularly the peaks at higher temperatures, particularly in the vicinity of 160 and 210 K. As a result, a total of TSL curve shifts to the region of higher temperatures (Fig. 6).

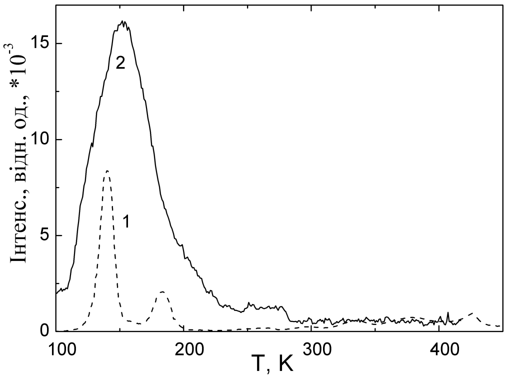

Fig. 6. Curves TSL compounds Zn2P2O7 (1) and Zn1,04Mn0,96P2O7 (2)

For TSL zinc monophosphate can spend depth evaluation of basic levels of capture, which correspond TSL peaks at 140 and 184 K.

Analysis of these peaks form shows that they are more extended by low temperatures, which is known to be a sign of so-called linear kinetics TSL (the probability of re-capture traps electrons in much smaller probability of recombination centers to glow). Taking into account this circumstance depth Et traps can be evaluated from the known elementary formula:

$$E_t = \frac{2T_m^2}{\delta} ,$$

where Tm - the maximum position, and δ - peak curve halfwidth TSL. Obtained by this formula values are ~ 2100 and 2500 cm-1, respectively, for peak at T = 140 and 184 K. As is known, the above formula for Et gives values inflated by 20 - 40% compared with the real, and therefore valid Et value should be measured values 1500 - 1750 and 1780 - 2080 cm-1.

Thus, both types of compounds without manganese and Magnesium have a similar system defects (traps). This system is obviously very complicated, which leads to different compounds review certain kind of excitement for different types. Thus, the energy of near UV light (eg, 337.1 nm) in compounds with Magnesium effective at low temperatures gets to red glow centers than to their own luminescence centers, and therefore in the PL spectra at low temperatures observed only red stripe, while at ambient temperatures of its intensity is very low (see. Fig. 1 and Fig. 2). When high-energy VUV excitation, which obviously causes interband transitions in the spectra doped compounds, regardless of the temperature samples mainly find long-wavelength red band radiation, and luminescence matrix - is missing. Obviously, at low temperatures, as in "nyzkonerhetychnomu" UV excitation when free charge carriers are formed, and at VUV excitation energy of excitation of the matrix effectively transmitted to the impurity ions of manganese, ("direct" excitement centers red luminescence possibly takes place). From this it follows that the UV and VUV excitations in luminescent processes involved defects that directly interact with the red luminescence centers. This, however, should be defects of various types, which differ provision of energy levels. Those of them that form deep levels, are more efficient at VUV excitation and defects of shallow levels in the current UV excitation. In the presence of manganese, at low temperatures, the excitation energy is transferred from defects mainly on luminescence centers, connected with the manganese ions and only when the temperature to ambient excitation energy defective matrix and transmitted to the centers own glow. Location defect levels at different depths varying temperature behavior causes red luminescence depending on the type of excitement "high-energy" VUV or "low-energy" UV excitation. As a result, the UV excitation of red luminescence decays rapidly with increasing temperature at VUV excitation - fading is slow. The above changes TSL curves (Fig. 6) showed that as a result of doping manganese zinc phosphate ions generated traps with deeper levels. When the X-ray excitation formed by free carriers is obviously better admire traps directly related to manganese ions than with their own luminescence centers, so that at low temperatures the intensity of the red luminescence intensity significantly exceeds its own glow. The depth of the traps as shown above calculation results is just one that can provide strong at room temperature attenuation Red RL RL and strengthen their own (Fig. 3).

The introduction of the manganese ions diphosphate zinc leads to change, obviously, not only in the ensemble of defects in the crystal lattice. These data indicate that based on ion manganese forming new impurity centers luminescence which should be associated emission bands in the range 450 - 650 nm (see. Fig. 1 and Fig. 2) and a strip of red emission with a maximum in the vicinity of 700 nm (see. Fig. 2 and Fig. 3). Indeed, there is generally known that the "green" glow in the range of 400 - 600 nm in compounds containing impurity manganese or manganese, which is included in their composition, can cause doubly charged ions Mn2 + in oxygen environment close to tetrahedral and ions Mn2 +, which are in octahedral oxygen environment, characterized by red luminescence in the range of 600 - 800 nm [1-6]. In complex matrices composed of complex oxide molecular anions, sometimes simultaneously detect both types of centers. The above data indicate the possibility of implementing this situation and investigated phosphates.

Simultaneous formation of manganese ions based centers of different types - octahedral and tetrahedral in the environment follows from the data structure diphosphate zinc and manganese. It is believed that Zn2P2O7 for zinc coordination number is 5 or 6 [9]. Such uncertainty can be seen as a consequence of the existence of a matrix diphosphate zinc polyhedra containing zinc ions, preferably with the number of oxygen atoms, four and six. This opportunity, in our view, have caused the original structure of the crystal lattice Zn2P2O7, in which there are two non-equivalent atoms of zinc, and if one of them has the ability to lose more easily than the other two oxygen atoms, the lattice oxygen polyhedra will exist mainly two types. It is possible that to some extent the structure of the lattice and polyhedron are presented with five oxygen atoms, which can be regarded as defective octahedron.

If manganese ions surrounded by four oxygen atoms are centers of "green" luminescence, the luminescence characteristics of those who are in the middle of the five polyhedra with oxygen, may be close to those of octahedral centers. Red luminescence analysis confirms that the observations we really red radiation is complex.

In - First, it points to a different temperature behavior of red radiation depending on the type of excitation, UV, VUV or X-ray. In - the second band of radiation at different types excitations although they are very close to the position of the maxima, but markedly different form bands. Thus, the VUV excitation circuit band (curve 1 in Fig. 3) describes one broad (δ = 1770 cm-1) Gaussian curve shape of □m cm-1 (λm = 696 nm); UV excitation leads to asymmetric curve (curve 2 in Fig. 2) which dominates much narrower (δ = 1120 cm-1) component Gaussian shape with □m = 14,580 cm-1 (~ 686 nm) with another term long-wave circuit : □m cm-1 (λm = 730 nm); δ = 640 cm-1). In X-ray excitation spectrum (curve 3 in Fig. 3) also have the sum of two Gaussian contours with maximum at 14,425 cm -1 (693 nm) and 13690 cm -1 (730 nm) and half-width of 990 and 1490 cm-1. Schedule these spectra into components shown in Fig. 7.

Formation of polyhedra with the number of oxygen atoms least six means of existence in the crystal lattice of a number of oxygen vacancies, which may be centers of their own luminescence cores diphosphate. From these data it is clear that the ratio of defects and impurity centers of radiation caused Magnesium influences the luminescent properties of the investigated compounds. Important is the very type of defect, which may vary competitiveness excitation energy channels: the centers own glow (fading), or to impurity luminescence centers.

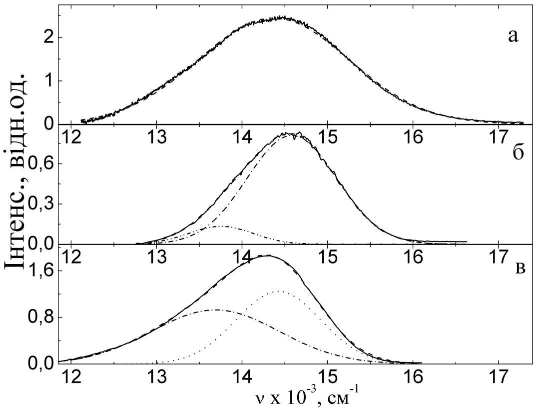

Fig. 7. Schedule luminescence spectra on Gaussian components: a) UV excitation, spectrum 2 in Fig. 2; b) at VUV excitation, spectrum 1 in Fig. 3; c) X-ray excitation: 3 spectrum from Fig. 3

Conclutions

The results suggest that the impurity ions of manganese, Mn2 +, in a matrix of zinc diphosphate form three types of radiation centers: Mn2 + in octahedral surroundings, these centers should be the majority; Mn2 + ions with defects in the form of oxygen vacancies in their octahedral environment and Mn2 + ions in tetrahedral environment. From the center of the first type is associated with a band of red emission peak in the vicinity of 690 - 700 nm, which prevails in all spectra; centers of the second type causing long-wavelength band of red light (maximum in the vicinity of 730 nm); strip "green" emission should correlate with the centers of the third type. Defects different type than oxygen vacancies in the first coordination sphere manganese ions and remote defect apparently causes non-uniform expansion strips red radiation.

One of the factors that may affect the properties of luminescence processes can certainly be water molecules, atoms which may be part of the inner circle of divalent metal lattice. So in part 2 of this paper will be considered the main manifestations of the impact of water on the luminescent properties of compounds Zn2xMnxP2O7.