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INFLUENCE OF COPPER IONS ON RECOMBINATIONAL PROCESSES IN KDP

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It is investigated TL of the crystals KDP doped by cooper ions. The cooper ions occupy cationic units or interstitial depending on a way of activation. It is established the Cu^{2+} as ions replacement and interstitial raise thermal stability of a matrix defects and give new peak TL at 140K. The presence of replacement ions Cu^{2+} in a lattice KDP results in occurrence of the new TL peak with a maximum at 240K. The assumption is made, that it is connected to formation of the centres Cu^{+}.

Keywords: crystals KDP, TL curve, doze irradiation, optical density, thermal stability, thermal activation.

The crystals of potassium dihydrogen phosphates (KH_2PO_4 or KDP) concern to group of materials with nonlinear optical properties and widely are used in laser engineering. The analysis of the literary data has shown that last decade number of researches of the radiation induced processes in these crystals essentially has increased. It is connected that the sharp deterioration of the operational characteristics of the given material is observed. It is caused by formation of the defects and coloration. One of the methodical approaches of study of radiation induced processes in crystals is introductions in them of impurities ions. The ions of transitive metals in KDP crystals have the special interest. It is known, that the ions of manganese enter into a crystal lattice of potassium dihydrogen phosphates by various ways [1]. It was established by EPR method. Depending on conditions they occupy mainly cationic sites or enter in interstices. The ions Cu^{2+} have the external electronic environment of kind d^9. Hence, on the electronic structure they can be attributed to transitive metals.

The choice of the ions Cu^{2+} as impurity is caused by that they enter into a crystal lattice of KDP by various ways. In work [2] it is shown by method EPR, that at doped KDP by $Cu(NO_3)_2$ the ions Cu^{2+} occupy mainly cationic sites, and at doped with the help of the salt $CuSO_4$ the ions of two valence copper occupy the interstices. It allows putting tasks on study of influence the impurities ions occupying various sites a crystal lattice on radiation induced processes. The decision of similar tasks allows receiving the additional information on a role of the structural factor on properties of crystals.

The exit of recombination luminescence carries the information on processes of accumulation the stable radiation defects. It is known [3] that before radiation damage of a crystal lattice it can essential to change processes of formation and accumulation of structural defects by ionizing radiation.

The crystals KDP doped by copper ions were brought up from the sated water solutions by a method of isothermal evaporation of the solvent at 40°C. For doped of samples in an initial solution the salt Cu $(NO_3)_2$ and $CuSO_4 \cdot 5H_2O$ in quantity 0.2 mol% were added. Such concentration of impurities in solution provides entry of Cu^{2+} ions in a crystal lattice KDP mainly in cationic or in interstices sites, accordingly. At increase of impurity concentration in a solution it is broken [2]. In result in both cases the monocrystals were received and it has appreciable colorings.

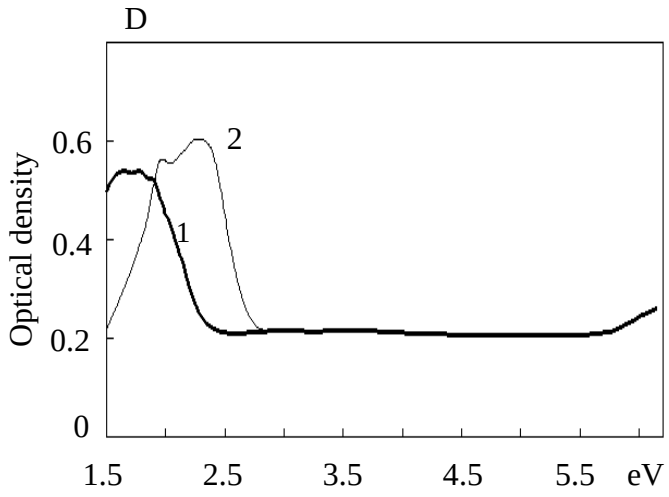

Fig. 1 Absorption spectrums for crystals KDP- $Cu(NO_3)_2$ (1) and KDP- $CuSO_4$ (2) at room temperature

In figure 1 the spectra of absorption measured at room temperature are submitted. The crystals KDP-$Cu(NO_3)_2$ have wide practically unstructured band of optical absorption, which begins below 1.5 эВ. In pure crystals and doped by ions NO_3^- of a similar of the absorption band is not present. Hence, it can be connected with impurity by ions Cu^{2+}. The wide unstructured of absorption band in long-wave range of spectrum are available, for example, in crystals sulphates of alkaline metals [4]. Occurrence of these absorption band is connected with d-d transitions.

In crystals KDP- $CuSO_4$ the optical absorption bands lay in a range from 1.5 эВ up to 2.5 эВ. It is obvious not elementary. The measurements of crystals KDP doped by ions SO_4^{2-} have shown, that this absorption bands is connected with impurities ions of two valance copper. Thus it is received, the same impurities ions Cu^{2+} in a lattice KDP has various absorption spectra depending on a type of salt, which was used. Hence, the ions Cu^{2+} occupy in a lattice KDP different sites. It will be coordinated to results of work [2].

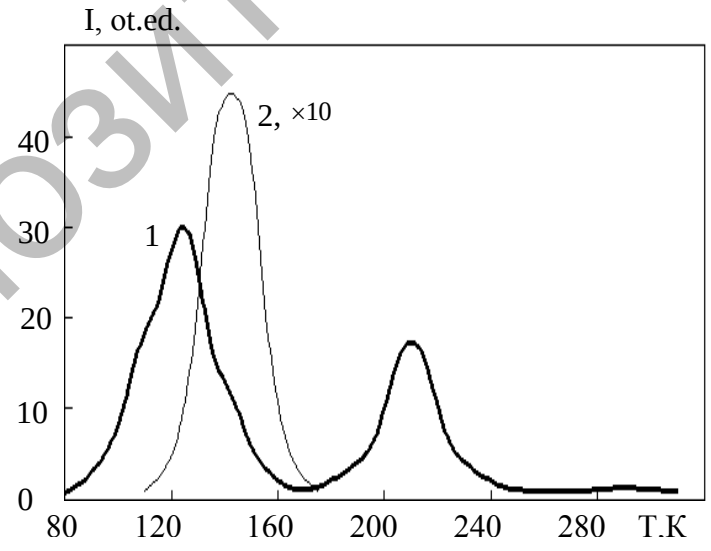

Fig. 2 TL curve for crystal a KDP-$CuSO_4$. Doze irradiation is 100 kGr

In figure 2 (the curve 1) is given a typical curve thermo luminescence (TL) for KDP-$CuSO_4$. The doze of an irradiation of x-rays at 80K is 100 kGr. At comparison given curve TL from a curve TL for a crystal KDP-K_2SO_4 [6] it is received, that the activation by Cu^{2+} ions results in occurrence of one new peak. It is shown as «shoulder» on high-temperature wing of TL peak with a maximum

about 125K. Isothermal tempering of the irradiated sample at 120K allows allocating it obviously (curve 2 figures 2). It has a maximum at 140K. Its spectral structure has a single band of emission with a maximum at 2.6 эВ. The suppression of accumulation lightsum in TL peaks of a matrix at 180K and 290K is connected to presence of the impurities sulphate anions, as well as occurrence of peak TL at temperature 210K [6]. The sharp increase of exit recombination luminescence is abnormal in area above 120K. This phenomenon communicates by us with reduction of activation energy as a result of polymorphic phase transition.

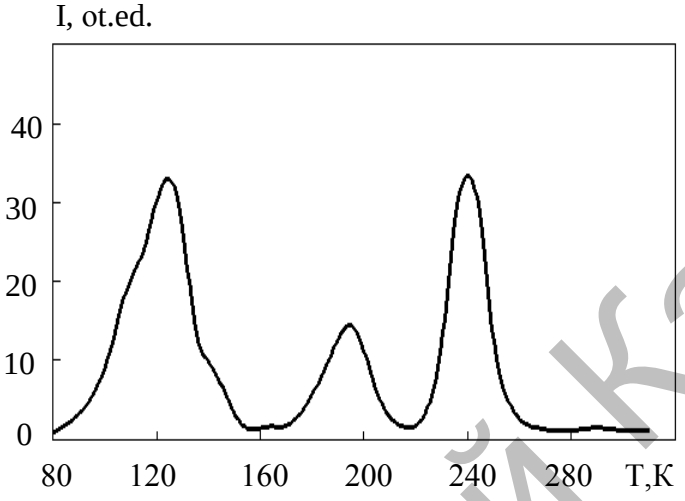

Fig. 3 TL curve for crystal a KDP-Cu$(NO_3)_2$. Doze irradiation is 100 kGr

In figure 3 the result of TL measurement for a crystal KDP-Cu $(NO_3)_2$ is submitted. The comparison of the given TL curve with TL for a crystal KDP-KNO_3 [6] shows, that the introduction of ions меди in this case results in occurrence of two new peaks. First is shown as «shoulder» on a high-temperature wing of TL peak with maximum at 125K, second peak has maximum at 240K. As well as in a crystal KDP-KNO_3 the own peaks of recombination luminescence at 180K and 290K are strongly suppressed and there is a peak of a luminescence with a maximum at 195K connected with presence in a sample of the anions NO_3^- [6]. Here as the abnormal increase of the luminescence exit is observed in the field of temperature Curie.

At isothermal tempering of irradiated with x-ray KDP-Cu $(NO_3)_2$ crystal at 125K the new TL peak with a maximum is allocated at 140K. The similar peak TL was found out in KDP-KSO_4 [6].

It was established for crystals doped by various copper salts, that the TL peak with a maximum at 140K has an identical spectrum of emission. It represents a single band with a maximum at 2.6 эВ. Thus it is established, that the temperature position of this new TL peak and its spectral structure does not depend on presence in KDP of the impurities anions NO_3^- or SO_4^{2-} and from position of Cu^{2+} ions in a crystal lattice. It allows approving, that the occurrence of TL peak at 140K on the one hand is connected to presence of copper ions; on the other hand its properties do not depend from Cu^{2+}.

We assume, that impurities copper ions raise the thermal stability of radiation defects of KDP crystals which break up in temperature area 100-130K. The TL peaks with maximums at 125K and 140K are caused by recombination processes of same nature.

It is assumed in work [7] that doped crystal by ions Mn^{2+} there is an increase of thermal stability at a part of Bjerrum defects. Unfortunately in the given work it is not described how the monocrystals KDP doped by manganese ions were received. It is known [1] the ions of manganese can enter into a crystal lattice KH_2PO_4 as an impurity of replacement and as interstitial ions. The ions of manganese concern to ions of transitive metals. To this to group, as it was specified above, it

is possible to attribute Cu^{2+} ions. Therefore assumption of increase of thermal stability at some defects of a matrix by copper ions is represented rather reasonable.

In a crystal KDP-Cu$(NO_3)_2$ the TL peaks with a maximum at 240K have the same band of emission, as own peak of a luminescence from pure KDP at 180K and peak in KDP doped by ions NO_3^- at 195K [6]. It allows approving, that the ions Cu^{2+} are traps for электронов in KDP.

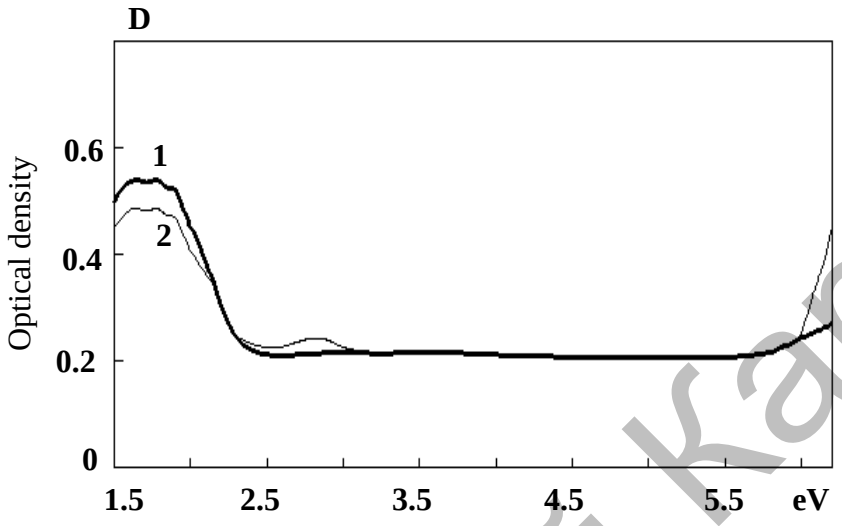

Fig. 4 Absorption spectra at 80K for KDP-Cu$(NO_3)_2$ before (1) and after (2) irradiation by x-ray. The curve 2 was measured after isothermal tempering at 140K

In figure 4 the spectra of absorption for a crystal KDP-Cu $(NO_3)_2$ are given at temperature of liquid nitrogen before and after irradiation of a sample by x-rays. It is visible from figure that after an irradiation the optical density of impurity absorption band decreases. The reduction of absorption has a unique explanation: the excitation of samples of high-energy quantums results in change of a charging condition at part impurity ions. Besides there is the new band of optical absorption in area is higher 6 эВ, which edge was observed by us. In crystals KDP-KNO_3 after an irradiation of the radiation induced bands of absorption in area higher 6 эВ is not present. Hence, the given optical band is connected with radiation induced impurity centers. It is formed in result changes of a charge on the Cu^{2+} ions.

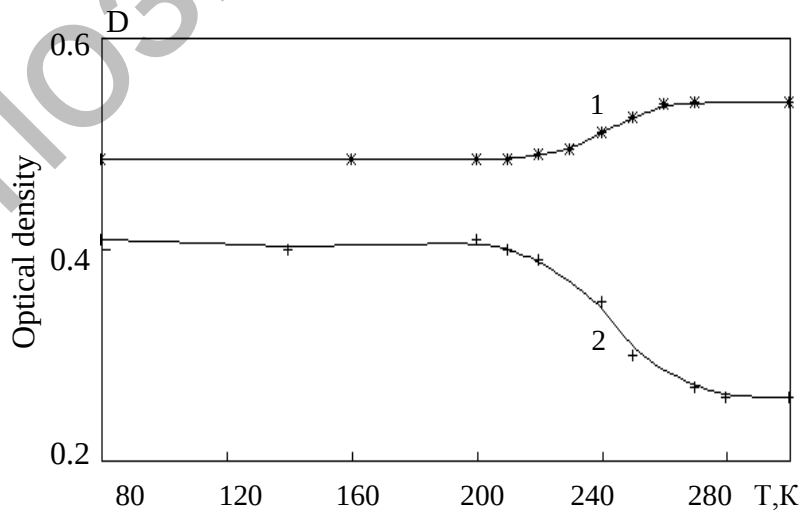

Fig. 5 Temperature dependence of optical density in the absorption band 1.75 eV (1) and 6.15 eV (2)

In figure 5 the curve dependences of optical density from temperature of heating of KDP-Cu $(NO_3)_2$ crystals are shown after irradiated by x-rays at 80K in band of the impurity absorption and radiation induced absorption band. From the received results it is visible, that restoration of concentration ions Cu^{2+} and tempering of the radiation induced absorption band occur synchronously in same temperature range 230-250K. Hence, the TL peak with a maximum at 240K is caused by thermal activation of disintegration radiation induced impurity centres.

We consider that as a result of an irradiation there are ions Cu^{+}. At ions Cu^{+} the valence environment is formed by ten d-electrons, i.e. the d-environment is completely filled. The electronic transitions in the lowest s-level are forbidden. The transitions in more highly laying electronic levels are solved. For example the absorption band of ions Cu^{+} in alkali halides crystals lay in area more than 5.8 эВ [8]. Besides experimentally it is established, that the ions of replacement Cu^{2+} essentially increase speed of accumulation light sum in low temperature TL peak of a matrix. The spectral structure of TL peak with a maximum at 240K has one band emission with a maximum 3.6 эВ. It coincides with emission in TL peak of a matrix at 180K. As in area 240K there is a disintegration of the radiation induced impurity centres it is impossible to consider, that the ions Cu^{2+} stabilize defects of a matrix, which are responsible for TL peak a maximum at 180K. The assumption of that impurity replacement ions Cu^{2+} in KDP are traps for electron does not contradict all set of the available facts.

Thus, the replacement and interstitial ions Cu^{2+} raise thermal stability of defects of a matrix, which disintegration in pure crystals gives a luminescence in area 100-130K. Besides the presence of the replacement ions Cu^{2+} in a lattice KDP results in occurrence of new TL peak with a maximum at 240K. The assumption is made, that it is connected to formation of the Cu^{+}.

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