

Effect of transition metal ions on the radiation and recombination processes in the crystals of KDP

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Abstract. This article presents the results of the study of the influence of impurity ions Co^{2+} , Ni^{2+} , Mn^{2+} , as well as sulfate anions on the radiation and recombination processes in crystals of potassium dihydrogen phosphate (KDP). The observed changes might be connected with the fact of crystals having Me^{2+} and SO_4^{2-} impurity ions. A model of the recombination process in the crystal KDP- K_2SO_4 at 210 K is offered. There was a proposition of the possibility of selective creation of impurity centers with the help of using various salts is normal for all the transition metal ions.

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Introduction

Dielectric crystals are considered as one of the most important construction materials in modern technology. The area of their usage keeps on expanding and the exploitation rules are becoming more and more complicated. The following problems which appear after this require a behavior forecast of construction materials in extreme conditions and modification of physical properties or creation of new materials with specific features.

Research objects in this case refer to single crystals of potassium dihydrogen phosphate (KH_2PO_4 or KDP) and activated crystals KDP- Co^{2+} , KDP- Ni^{2+} , KDP- Mn^{2+} , KDP- K_2SO_4 .

KDP crystals maintain nonlinear optical properties. Some modern devices have found the usage to various single crystals from KDP [1]. The simplest method to change optical, mechanical or electrical properties of crystals is introduction of various substitution impurities or ionizing radiation exposure. However, the targeted modification requires deep understanding of the interaction process between radiation and a substance. Creating crystal lattice defects which happen as a result of radiation and chemical processes are considered to be the most striking manifestation to the statement above. The knowledge of their creation and conversion allows doing a research on radiation resistant and radiation sensitive materials which are used as construction components in various technology areas.

As a result of electron paramagnetic resonance and optical research methods, the number of defects in KDP crystals are as followed: B-radicals which represent self-trapped holes (H_2PO_4^0) [2, 3]; A-

radicals which represent self-trapped holes with hydrogen vacancy (HPO_4^-) [4]; PO_3^{2-} ions; interstitial hydrogen atoms [5]; Bjerum's L- and D-defects [6].

The analysis of published data on optical and radiation properties of KDP crystals and their identical combinations shows the lack of the research. Nowadays, by using various methods, KDP crystals have the number of radiation defects being set. However, their creation and recombination mechanisms are hardly discussed. The only mechanism, which has been thoroughly discussed and justified, is capturing electrons with bridging protons with following non active exit of hydrogen atoms in the interstices [7]. Obviously, B-radicals appear as a result of anion ionization. The creation of A-radicals is connected to ionization of L-defects which obtain pre-radiation substance or appear in the capture of the electrons. These processes are realized at the stage of the crystal radiation ionizing process. However, it is well-known [8] that, A-radicals are formed at post-radiation stage. The given processes are not discussed in modern technology. There are no scientifically proven concept models about recombination process mechanisms, except general statements on electron and holes recombination without confirmation of the nature of their carriers.

Transition metal ions are one of the traditional activators to study the spectral luminescence and radiated properties of crystals. According to the literature while as influence of transition metal ions on radiation stimulated processed in potassium dihydrogen phosphate are discussed regularly.

Objects and methods

The growth of KH_2PO_4 single crystals was produced of saturated aqueous solutions using isothermal evaporation of the solvent at 40°C . Given temperature conditions of growth were taken from research work [9]. 10-12 days after this process, there were 5 mm to 40 mm sized crystals distracted from a saturated KDP solution. Sizes of the ready crystals radically vary depending on the components added into the final impurity solution. Activated single crystals were received after soluble metal salts were added to the final solution. Usually, concentration of the components added to the final solution is around 0.1 mol%.

Our work in particular included measurements of the absorption spectra of the luminescence excitation and emission at different temperatures which were used from the optical research methods. Absorption spectra of crystals and induced absorption spectra in the area of 200 – 800 nm were measured using photoelectronic method on spectrophotometer SPh-16 by standard methods [10]. Measuring optical density of the crystals was done relating to the air. Additional absorption spectra were measured towards non-radiated crystals. Although, the certain number of situations involved using slightly radiated crystals. The last one took place to learn the influence of ionizing radiation on impurity absorption. Measurement of the absorption spectra was done at 80 – 320 K temperature range. The sources of light varied depending on the spectra range, starting with incandescent lamp ending with DDS-30 hydrogen lamp.

In all the optical measurement procedures, the research object was put into a nitrogen cryostat and then was cooled down to the temperature of liquid nitrogen and radiated with X-ray through beryllium window of URS-55a device. X-ray tube had a molybdenum anode. Measuring crooked thermo luminescence was done by supporting the constant speed of the heat in 9 K/min, which was controlled with the help of the differential copper-constantan thermo steam.

To define the absorbed dose of the X-ray radiation we used Frike chemical dosimeter. Dosimeter readings do not depend on power of the absorbed radiation dose up to $10^5 \text{ Gy}\cdot\text{s}^{-1}$. Accuracy of Frike dosimeter measuring is approximately $\pm 5\%$. As a result of the produced measurements it is defined that the power of radioactive dose from URS-55a X-ray device with X-ray tube and copper anode at the voltage of 35 kV and current of 10 mA makes about $150 \pm 10 \text{ kGy}\cdot\text{s}^{-1}$.

Results and discussion

Fig. 1 represents the typical TSL curve for pure potassium dihydrogen phosphate crystals with the radiated dose of X-ray quanta at the liquid nitrogen temperature 40 kGy [11, 12]. The image shows that there are three TSL peaks with the maximum points at 110 – 130 K, 180 K and 290 K.

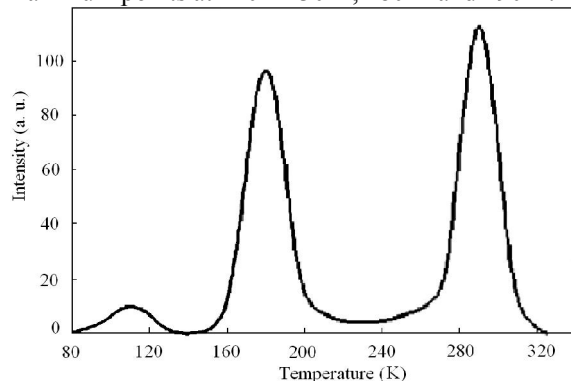


Fig. 1. TSL of potassium dihydrogen phosphate

Comparison of thermal bleaching curves of radioactively navigated absorption bands and electron paramagnetic resonance (EPR) [8] spectra temperature dependence intensities allowed to do the correlation of radioactively navigated absorption bands with matrix defects. At 80 K, the appearance of radioactively navigated absorption bands is caused by B-radical typed defects and interstitial hydrogen atoms. The correlation of the details mentioned above with the crooked TSL allows confirming that the peak in 110 K – 130 K area is connected to the destruction of B-radicals, and the maximum at 180 K is connected to the destruction of A-radicals. In both recombination processes they use the atomic hydrogen which plays the role of electron-overload defect. In 110 – 130 K area the recombination process mechanism is holed, whereas 180 K area it is electron based [11]. There is a proposition that the TSL peak at the maximum of 290 K is somehow connected to the destruction of PO_3^{2-} defects.

It is known [13] that Cu^{2+} ions take various position in KDP crystal lattice. With addition of CuSO_4 salt to mother solution for KDP activation, metal impurity ions take interstitial positions, whereas by adding $\text{Cu}(\text{NO}_3)_2$ – cation sites. In the given work [14], it was proven that by using EPR that Mn^{2+} paramagnetic center spectra in KDP crystal lattice thoroughly change depending on the metal salt used as an activator. Authors of the given work assure that it is connected with various positions of bivalent manganese ions in KDP crystal lattice. As analog to the impurity ions of bivalent copper, Mn^{2+} ions are either substitutive impurities or take interstitial positions.

Fig. 2 shows traditional TSL curves for KDP crystals, activated by MnSO_4 , NiSO_4 and CoSO_4 .

Radiated dose – 150 kGy. Comparison of experimental results shown on Fig. 2 alongside with the TSL curve for a pure KDP on Fig. 1 shows that recombination processes in activated crystals are doing some noticeably rapid changes.

There are some new TSL peaks in crystals with bivalent manganese impurity ions in areas of 140 K, 210 K and 230 K (Fig. 2, curve 1). The peak of glowing at 140 K appears in a shape of a “shoulder” on a line of the burning of recombined luminescence with the maximum of 180 K, which is usual for matrix. At the area of 100 – 130 K there is an expressed maximum glow factor at 100 K. In pure KDP crystals the lightsum of recombined glow at this temperature range is not severely noticeable. The activated KDP-Mn²⁺ crystal obtains the light sum of the low temperature peak which is noticeably more towards the matrix peak at 180 K.

In crystals with bivalent cobalt impurity ions (Fig. 2, curve 2) there is a new peak in the TSL at 140 K which is clearly defined. TSL peaks which are considered normal for the matrix with maxima at 180 K and 290 K are slightly suppressed. The low-temperature peak of the recombined luminescence has a maximum at 110 K. Lightsum of the peak of the glow curve for the TSL is dominant.

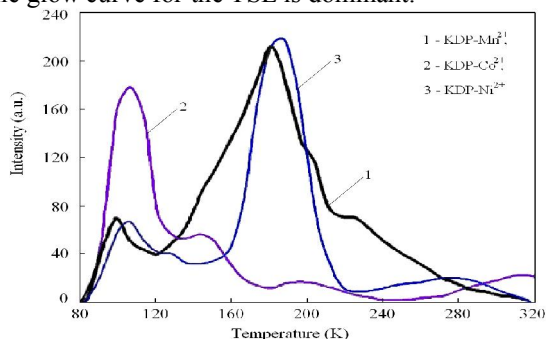


Fig. 2. TSL curves for activated KDP crystals

In crystals with bivalent nickel (Fig. 2, curve 3), a new peak in the TSL appears as a “shoulder” in the high-wing emission peak with a maximum at 110 K. Thermal annealing carried out at 100 – 110 K for pre-irradiated X-rays of the sample allows selecting a new peak emission. It is a maximum of 140 K. TSL peak, which is normal for the matrix with maxima at 290 K, is depressed. Recombined luminescence peak with maximum at 190 K is dominant at accumulated lightsum.

KDP crystals, which were grown by adding 0.1 mol% (Fig. 3, curve 1), 0.2 mol% (Fig. 3, curve 2) and 0.5 mol% (Fig. 3, curve 3) of potassium sulphate to the final solution, had optical absorption spectra measured at the room temperature.

During the concentration growth of potassium sulphate in the final aqueous solution of

KDP, TSL matrix peaks suppress at 180 K and 290 K maximum unit points (Fig. 3). KDP-K₂SO₄ crystal was radiated by X-ray quanta at liquid nitrogen temperature first, then isothermally burnt at 180 K. As a result we got a new TSL peak with a maximum of 210 K, which we connect with the samples having impurity sulphate anions. It is clear that the radiation spectra of TSL at the maximum of 210K consist of two radiation lines (Fig. 3, b). Their maximum points are at 2.6 eV and 3.6 eV. 3.6 eV of radiation is considered normal for matrix and monitored in X-ray luminescence spectra as well as in recombined glow radiation spectra, which can obtain the maximum of 180 K. The second radiation band serves as a proof to the fact that KDP-K₂SO₄ crystals have a more complicated recombination process at 210 K.

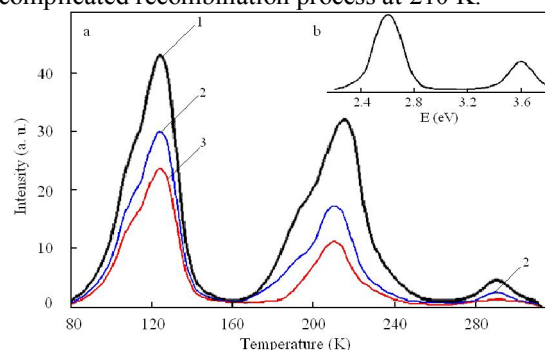
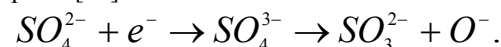


Fig. 3. (a) TSL curves for KDP-K₂SO₄ and (b) spectral composition of TSL peak at 210 K

Research of radiation stimulated processes in potassium sulphate shown that at the electron capture by SO₄²⁻ anions, activation less decay takes place [15]:



Oxygen ion plays the role of electron overload center.

The radiation band at 2.6 eV is considered normal for pure KDP crystals. It is observed at the low temperature measurements of X-ray luminescence spectra [16] and at the recombination of radiation defects at 110 – 130 K area. Dependence of X-ray luminescence on temperature in the radiation band with the maximum of 2.6 eV for KDP-K₂SO₄ crystal shows that the glowing of the given sample is experiencing temperature extinction in 80 – 170 K then 200 K and higher areas. TSL peak at 200 K explains the buildup of recombination luminescence at this area. In the pure KDP crystal the radiation band at 2.6 eV is also experiencing temperature extinction and above 170 K is practically not observed. So, this way, recombined luminescence of matrix at the maximum of 2.6 eV and the according radiation line at the TSL peak with 210 K have different consistency nature.

Alkali metal sulphate crystals have the radiation band at the TSL peak with the maximum of 2.6 eV. Its appearance is often related to the thermal activation of the oxygen atom migration with its following recombination with SO_3^{2-} defects.

According to [15] during the decay of SO_4^{2-} sulphate anion which happens as a result of dissociative electron capture, O^- ion stabilizes along with SO_3^{2-} . O^- ion is considered as the only defined electron overload center in alkali metal sulphates. The variation of the cation surroundings might have been a cause for creation of O^- electron center which obtains different levels of thermal stability, which leads to the appearance of a few TSL curve peaks connected with recombination processes of the same nature.

The closest anions surroundings in KDP crystal lattice is created with two hydrogen units. Electric charge almost equals +1 (in electron units). Hydrogen cannot stabilize an oxygen ion. It is more likely that OH^0 creation as a result of proton with the oxygen ion. It is possible to suppose that OH^0 decay happens at 210 K area, as oxygen and hydrogen atoms form. Oxygen atom recombines with SO_3^{2-} which gives luminescence at the maximum of 2.6 eV. Hydrogen atom works during the recombination with A-radicals, which gives luminescence at the maximum of 3.6 eV. The proposed model of the recombination process in KDP- K_2SO_4 crystal at 210 K area gives explanation to all the monitored occasions.

The having impurity sulphate anions in KDP crystal lattice lead to the storage of the glowing lightsum at the TSL matrix peaks with the maximum at 180 K and 290 K. Moreover, there is a new peak which comes to scene at 210 K. Compare TSL curves shown in Figures 3 and 4. There is no severe case of recombined luminescence peak at 210 K in the crystals activated by cobalt ions. Also, a slight glowing peak can be monitored at 180 – 220 K, only in case it is wrapped in a high temperature shield. For the crystal with nickel impurity ions, the temperature position of the glowing peak is positioned 10 degrees to the side of the high temperature shield. Moreover, a high temperature shield is wrapped according the temperature. Isothermal annealing at 180 K allows bringing out the glowing peak at 210 K from the KDP- NiSO_4 crystals, previously radiated with X-ray. Samples activated by manganese sulphates have the TSL peak in a “shoulder” form on the high temperature shield of second TSL matrix peak at 210 K.

From all the facts mentioned above, there is only one recombined luminescence appearance peak at 140 K which is related to the influence of

transition metal ions. Its observing does not depend on the nature of transition metal impurity ions.

To define the reason of recombination glow in 140 K, we have detected its spectra composition. As the given TSL peak is well monitored only in KDP- CoSO_4 crystals, the measurements were made only for these samples. Fig. 4 shows TSL curve for KDP- CoSO_4 and the spectra composition for TSL peaks at 110 K and 140 K. Spectra composition of TSL peak at the maximum of 140 K only contains one radiation line at 2.6 eV. In [12] research work there was also a TSL peak at 140 K observed; it was obvious in KDP crystals, which were activated with bivalent copper ions with the radiation line of 2.6 eV.

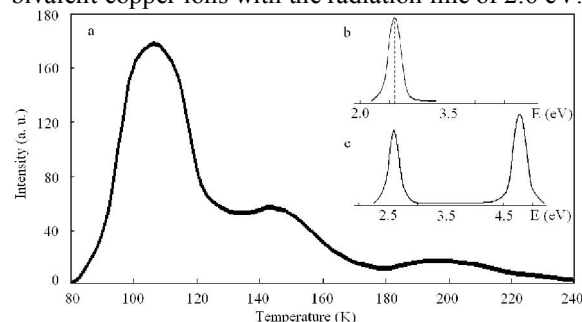


Fig. 4. (a) TSL curve for KDP- CoSO_4 and spectral composition of TSL peaks at (b) 110 K and (c) 140 K

Accordingly, this recombined luminescence peak and the radiation spectra composition does not depend on transition metal ions consistency nature. On one side, it appears whilst having the transition metals impurity ions, and on the other hand, its properties do not depend on this fact. This allows thinking that Me^{2+} ions change the level of thermal stability of matrix radiation navigated defects.

It is clear [2, 8, 17] that KDP pure crystals get colored under the ionizing radiation. Three observed absorption bands have the maximum points at 2.26 eV, 3.17 eV and 5.75 eV. The received results are as expected in the papers [8], according to which DKDP crystals have been detected to obtain radiation navigated absorption bands at 230 nm, 390 nm and 550 nm (5.39 eV, 3.18 eV and 2.25 eV). In [11] research work it is shown that radiation navigated absorption bands are conditioned with absorption in B-radicals at 2.26 eV, 3.17 eV and with interstitial hydrogen atoms at 5.75 eV. In KDP pure crystals there is a thermal self-trapped hole (B-radicals) activation, which takes place at 100 – 130 K.

Fig. 5 shows thermal bleaching curves for pure KDP and KDP- CoSO_4 , radiated at 80 K in the radiation navigated line with the maximum of 3.17 eV, which is related to B-radicals.

The Fig. 5 shows that the temperature dependence of the absorption band for the activated

crystal is different from that in a pure sample. The given outcome is considered as a direct proof to the fact that Co^{2+} ions increase the thermal stability of B-radicals in KDP crystals. Analogous outcome was received for KDP- MnSO_4 crystals.

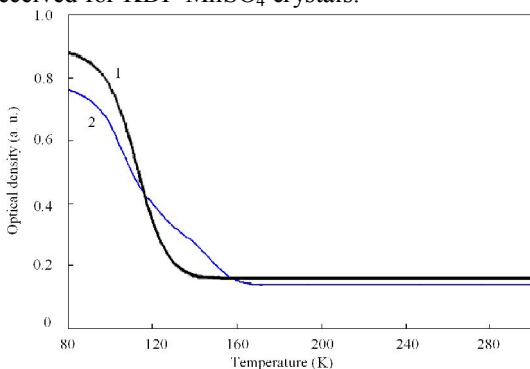


Fig. 5. Thermo bleaching curves in the absorption band, 3.17 eV: 1 – for KDP crystal, 2 – for KDP- CoSO_4 crystal

Conclusion

So, this way, the influence of impurity Co^{2+} , Ni^{2+} , Mn^{2+} ions and SO_4^{2-} anions on the formation, accumulation and recombination of radiation defects in KDP crystals are investigated. While as it is experimentally proven that K_2SO_4 -KDP crystals get colored after the radiation with X-ray quanta at 80 K. Introduction impurity sulphate anions in KDP crystal lattice lead to the storage of the glowing lightsum at the TSL matrix peaks with the maximum at 180 K and 290 K. The bivalent cobalt ions increase the thermal stability of B-radicals in KDP crystals, which leads to the appearance of TSL peak at the maximum of 140 K. Thus, the number of direct tests and measurements served as a proof that all the impurity ions of transition metals in interstitial positions lead to increasing the level of thermal stability for a certain part of radiation navigated B-radicals.

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