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Research of radiation impurity defects in the crystals of potassium sulphate activated by ions of the transitional metals

The radiation impurity defects in the crystals of potassium sulphate activated by ions of the transitional metals was research in this work. According to spectra of optical absorption of K_2SO_4–Co^{2+}, K_2SO_4–Mn^{2+}, K_2SO_4–Ni^{2+} crystals of research it is possible to draw qualitative conclusions on impurity and dot defects of objects. It is clear that after radiation by X-ray quantum the optical density in the impurity absorption bands of the crystals are decreases. This phenomenon is explained that there is a change of charging state at initial ions of divalent metal ions and the impurity ions either are ionized or are traps for electrons. It was found that the impurity ions of the transition metals Me^{2+} are the centers of electron capture in potassium sulphate.

Key words: ionic crystals, potassium sulphate, absorption spectrum, impurity ions, defect.

Potassium sulphate, as well as potassium dihydrophosphate is a crystal with the composite anionic complex. Due to the practical application of these crystals in the last decades specific features of characteristic and impurity electronic exaltations [1] are widely investigated. The role of anions is played by the complex formations — molecular ions of SO_4^{2-}, PO_4^{3-}, etc. In the row the oxianionic crystals the conduction area is formed from excited states of cations and anions. The valence zone of nonactivated crystal of K_2SO_4 consists of three subareas divided by the forbidden areas. While introduction of impurities into the crystal lattice in the forbidden area of diamagnetic crystals there are power subtotals which are caused by impurities. Owing to formation of power subtotals in the forbidden area in the range of optical absorption, shifted in the long-wave party from edge of fundamental absorption of the crystal [2]. According to spectra of optical absorption of objects of research it is possible to draw qualitative conclusions on impurity and dot defects of products of radiolysis in a crystal. Absorption spectra of the transitional metals of crystals of potassium sulphate activated by ions were for this purpose measured.

The crystal absorption spectrum K_2SO_4–Co^{2+} (Fig. 1) received at ambient temperature which is well coordinated with the result given in work [3].
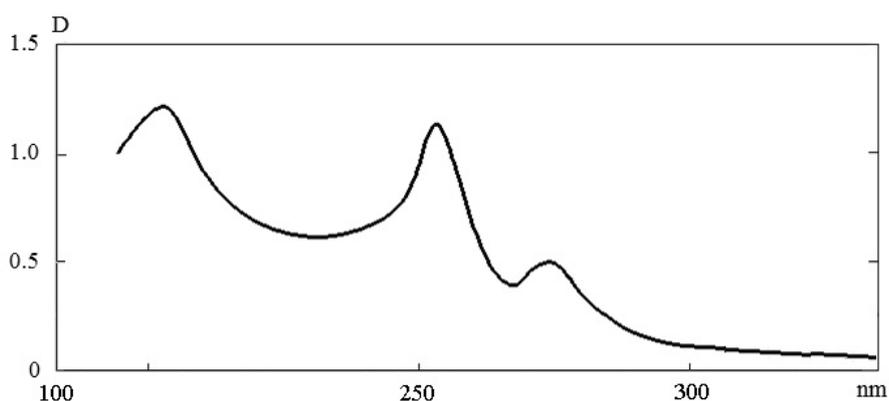

Figure 1. Crystal absorption spectrum K_2SO_4-Co^{2+}, measured at ambient temperature

From the Figure 1 it is clear that in the field of matrix transparence the impurity ions are resulted in emergence at ambient temperature of three new absorption bands with maxima at ambient temperature absorption bands at 271.33 nm, 250 nm and 212 nm are observed (see Fig. 1). In a clear crystal of potassium sulphate in this area absorption bands are not present and observed optical strips contact the impurity absorption. The optical density of absorption bands grows with body height of concentration of the impurity

centers that confirms their nature. At increase in concentration of Co^{2+} in potassium sulphate the new strip at 775 nm that is associated by authors [3; 2039] with the modular impurity centers. At temperature decrease there is a «blue» shift and there are new absorption bands. The increase in number of absorption bands at temperature decrease is bound to decrease of width of the optical strip that leads to manifestation of the splittings which are not observed at higher temperature.

At temperature decrease (from ambient up to the temperature of fluid nitrogen) the absorption spectrum of unirradiated crystal of K_2SO_4–Co^{2+} does not change qualitatively. While in the case of radiation of the crystal of K_2SO_4–Co^{2+} by X-ray quantums the new activated strip with a maximum at 234 nm appears. The absorption spectrum measured at 80 K for K_2SO_4–Co^{2+} crystal before radiation (curve 1) and after radiation (curve 2) by X-ray quantums with dose 500 кGy is given on Figure 2.
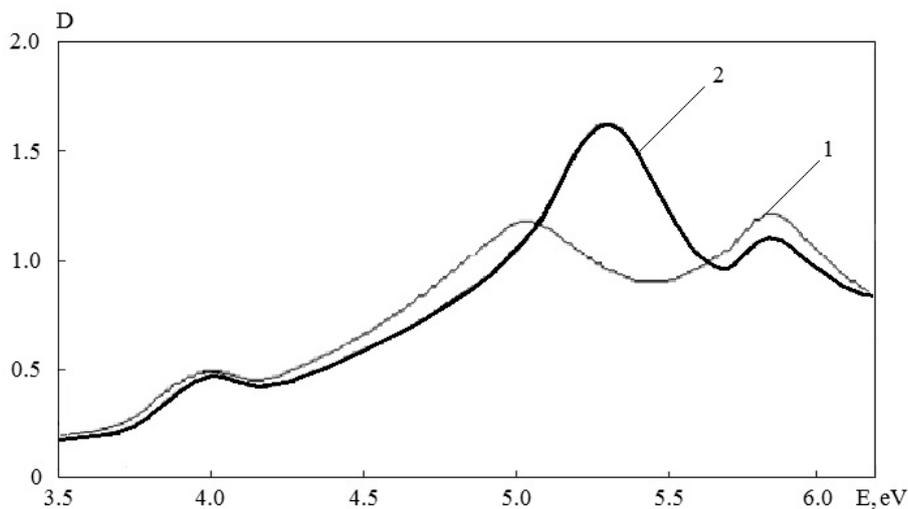

Figure 2. K_2SO_4–Co^{2+} crystal absorption spectra, measured at the temperature 80 K

From the Figure 2 it is clear that after radiation by X-ray quantums the optical density in the impurity absorption bands of the crystal of K_2SO_4–Co^{2+} decreases. It can be explained that there is a change of charging state at initial ions of divalent cobalt, i.e. there is formation of ions Co^+ or Co^{3+}. Besides, there is a new absorption band with a maximum at 5.30 eV. This radiation induced absorption band was observed in work [4]. In this work by means of the EPR method it was established that emergence of this absorption band is connected to the hole centers SO_3^-. As potassium sulphate crystals under the influence of radiation are not painted authors of work [4; 2040] connected it with the hole center of matrix, revolted with the impurity ion Co^{2+}. The similar phenomenon was observed in the crystals of potassium sulphate activated by Cu^{2+} ions.

The radiation induced absorption band in this exemplar is observed in the field of 5.61 eV [5]. In the crystals of potassium sulphate activated by Cu^{2+} ions new peaks of TSL are not present. Therefore, it is necessary to solve the issue of the nature of new peak of recombinational luminescence in K_2SO_4–Co^{2+} crystal with a maximum in area 240 K. This peak of luminescence can be connected with disintegration of indignant of the impurity ions of the hole centers of matrix, or to disintegration of the radiation induced impurity centers which education are proved by measurements in the impurity absorption bands after radiation of exemplars.

The absorption spectrum for K_2SO_4–Mn^{2+} crystal, received at ambient temperature is given on Figure 3. In this case at ambient temperature absorption bands at 4.0 eV and 5.04 eV are observed. The absorption band with a maximum at 5.04 eV is dominating. The absorption band with a maximum at 4.0 eV is non-elementary. On its long-wave wing there is «shoulder». Fall of temperature (from ambient up to the temperature of fluid nitrogen) the absorption spectrum for K_2SO_4–Mn^{2+} crystal also does not change qualitatively (Fig. 4). At low temperatures (80 K) non-simplicity of a long-wave optical strip is shown more obviously.

For definition of the nature of new TSL peaks of the crystal K_2SO_4-Mn^{2+} curve absorption before radiation were measured by X-ray quantums (Fig. 4). Here the decrease of optical density in the impurity absorption bands is observed. It testifies about decrease of a number of the centers of absorption in a crystal. This phenomenon is explained by change of charging condition of the impurity ions of the transitional metals. The impurity ions either are ioned, or are traps for electrons. Besides, after radiation in K_2SO_4–Mn^{2+} crystal

there is a new absorption band with a maximum at 5.5 eV. According to literary data [4; 2040] absorption with a maximum at 5.5 eV contacts defect of SO_3^- which is located about the impurity ion of Mn^{2+}.
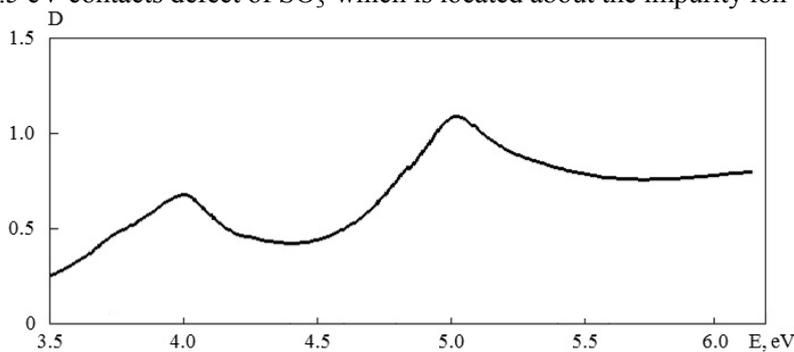

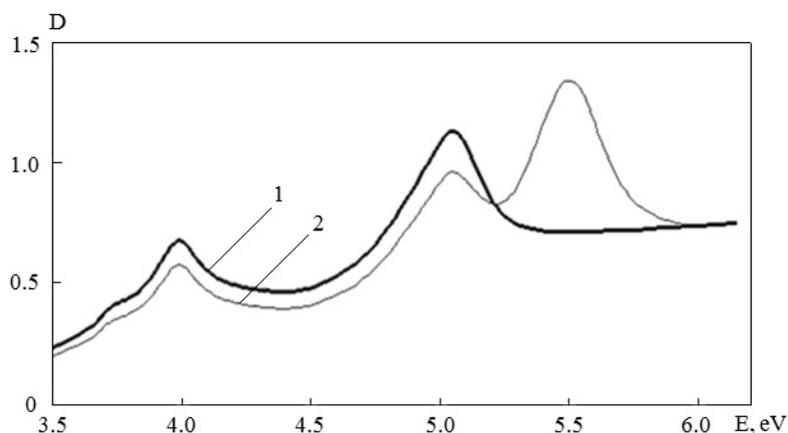Figure 3. K_2SO_4–Mn^{2+} crystal absorption spectrum +, measured at ambient temperature

Figure 4. K_2SO_4–Mn^{2+} crystal absorption spectrum, measured at a temperature 80 K

The absorption spectrum for the activated crystal K_2SO_4–Ni^{2+}, measured at ambient temperature is given in Figure 5. Crystal plates of different thickness were received by a serial co-grinding of one crystal. From Figure 5 it is clear that in the field of matrix transparence of the impurity ions lead to emergence at ambient temperature of two new absorption bands with maxima at 4,13 eV and 5,17 eV. More intensive absorption band begins from 5.17 eV and stretches into ultraviolet area. Less intensive absorption band has an absorption maximum approximately 4.13 eV. In accordance with [6] where there is this third peak for K_2SO_4–Ni^{2+}, with maximum at 2,95 eV in K_2SO_4-Ni^{2+} crystal absorption spectrum, measured at ambient temperature is available also the third absorption band which is weaker in its intensity in comparison with absorption bands with maxima at 4,13 eV and 5,17 eV. This circumstance contacts that the absorption band at 2,95 eV is observed only in crystals more than 2,5 mm thick.
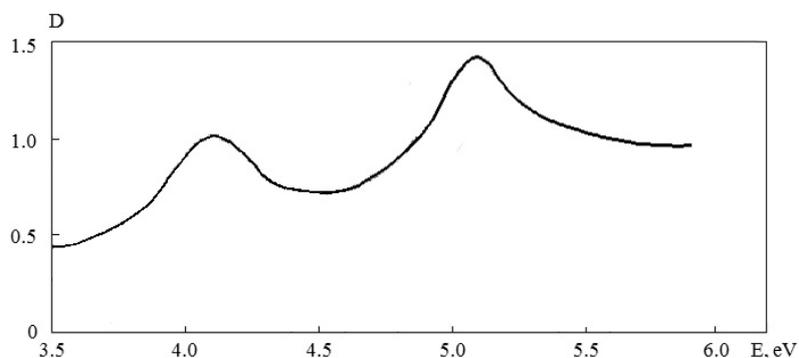

Figure 5. Crystal absorption spectrum K_2SO_4–Ni^{2+}, measured at ambient temperature

For consideration of absorption spectra K_2SO_4:Ni^{2+}, in approximation of the average crystal field it is necessary to know the electronic configuration of the ion Ni^{2+} — $3d^8$ The main term of the ion is the term ^3F. The nearest exited terms: $^3F(d^8)$, $^1D(d^8)$, $^3P(d^8)$, $^1G(d^8)$ и ^3F $3d^7 4s^1$. In K_2SO_4 lattice, in the assumption that Ni^{2+} ions replace any cations of the basis in cluster positions, the site is a symmetry of ions of Ni^{2+} — $C_s(\sigma_h, E)$. All electronic terms will be transformed on representations of A' and A''. Thus, each of orbital terms comprises both A', and A'' representation.

In the work [7] provided data on research of spectral characteristics of Ni^{2+} in the crystal of calcium iodide. In absorption spectra of CaI_2:NiI_2 wide activated strips with maxima in area 260–340 nanometers, bound to charge transfer, and the narrow activated strips observed on long-wave recession of strips of charge transfer, caused by d-d-transitions in Co^{2+} ions and Ni^{2+}, the haloid ions which are in an octahedral environment were found. Authors of work [7; 73] is established that Co^{2+} ions and Ni^{2+} do not form in iodide calcium of the luminescence centers radiating in the visible range of a range at x-ray exaltation, and are quenchers of a X-ray luminescence of the basis of crystals.

Consideration of absorption spectra K_2SO_4: Ni^{2+}, in approximation of the average crystal field, allows to assume that the front page of absorption corresponds to transitions from the A'(3F) level to one of levels splitted off configuration $3d^7 4s^1$ as its energy is closest to energy of transition $^3F(3d^8) \rightarrow$ $^3F(3d^7 4s^1)$. Much larger crystal fields are necessary to perform of d–d transitions. The second, intensive absorption band with a maximum at 4.13 eV probably corresponds to transition A'(^3F) $\rightarrow$ A''(^3P). In average crystal fields for performance of these transitions the necessary wavelength gets to the interval from 3.35 to 4.59 eV. Absorption bands in area 1.0–2.07 eV in crystals K_2SO_4–Ni^{2+} was not observed by us.

In Figure 6 K_2SO_4–Ni^{2+} crystal absorption spectra before radiation (curve 1) and after radiation (curve 2) at the temperature 80 K are given. From the figure it is clear that K_2SO_4–Ni^{2+} absorption spectrum has three peaks with maxima at 3.0 eV, 4.75 eV and 6.3 eV. While, the absorption spectrum with the maximum of 6.3 eV which contacts radiation of the crystal, is shown in the form of a shoulder in long-wave area 5.7–6 eV. From this drawing it is seen that at influence of X-ray quantums the charging condition of the impurity ions of Ni^{2+} changes.
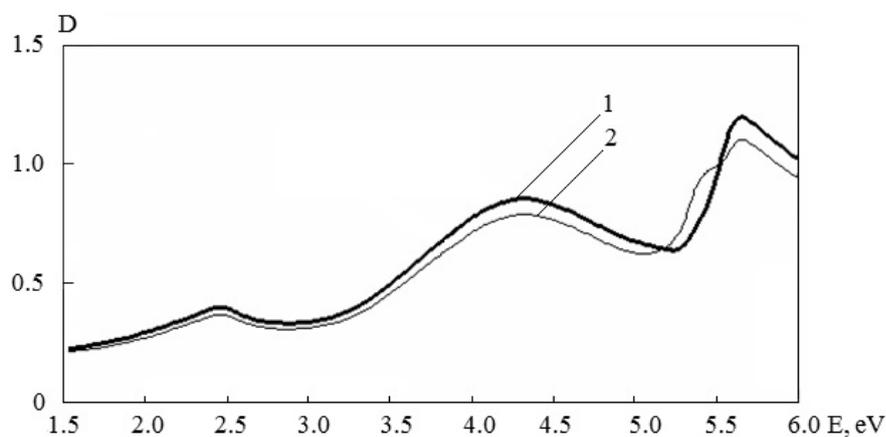

Figure 6. K_2SO_4–Ni^{2+} crystal absorption spectrum, measured at the temperature 80 K

In general, the influence of ions Co^{2+}, Ni^{2+} and Mn^{2+} on radiation and stimulated processes in crystal K_2SO_4 is similar. It can be proved by means of dependence curves of speeds of accumulation lightsum on the radiation dose in TSL peak at the temperature 190 K (Fig. 7). From Figure 7 it is clear that the impurity ions Co^{2+}, Ni^{2+} and Mn^{2+} increase the speed of lightsum accumulation in the TSL peak. Therefore, the impurity ions Co^{2+}, Ni^{2+} and Mn^{2+} in crystals of potassium sulphate are the efficient centers of capture for electrons.

1 — K_2SO_4; 2 — K_2SO_4-Co^{2+}; 3 — K_2SO_4-Ni^{2+}; 4 — K_2SO_4-Mn^{2+}
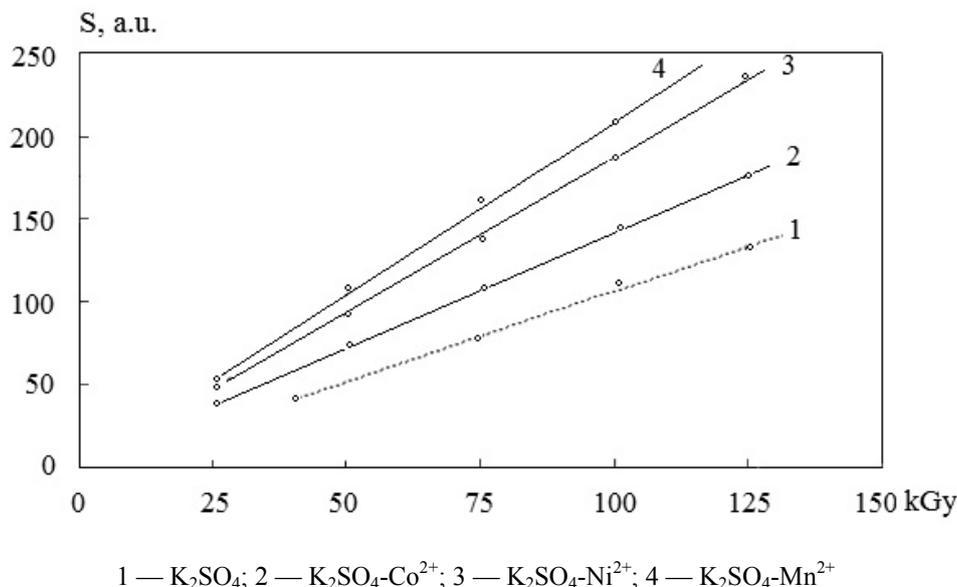
Figure 7. The dependence curves of speeds of accumulation lightsum on the radiation dose
in TSL peak at the temperature 190 K

The emergence of absorption bands in the crystals of potassium sulphate activated by Co^{2+}, Ni^{2+} and Mn^{2+} in the field of the matrix transparence according to [8] can be connected to the individual impurity centers. Exaltation of exemplars in these strips does not lead to emergence of photoluminescence. Measurement of photoconduction in a short-wave absorption band for K_2SO_4-Cu^{2+} crystal showed that it is not a charge transfer strip. Similar results were received for K_2SO_4-Ni^{2+} и K_2SO_4-Mn^{2+} crystals at exaltation in short-wave absorption bands. The activated -Co^{2+}, K_2SO_4-Ni^{2+} and K_2SO_4-Mn^{2+} the absorption spectra (Figures 1, 3, 5) measured at ambient temperature are qualitatively similar.

Thus, the impurity ions of the transitional metals Me^{2+} (Co, Ni, Mn) are the centers of electron capture in K_2SO_4. These impurity ions influence emergence of padding cationic vacancies in a crystal. The impurity anions (SO_4^{2-} and NO_3^-) in potassium sulphate are also traps for electrons.

References

1   *Ким Л.М., Кукетаев Т.А., Мусенова Э.К., Тагаева Б.С.* Влияние полиморфных фазовых переходов на свойства примесных ионов таллия // Хаос и структуры в нелинейных системах. Теория и эксперимент: Материалы 6-й междунар. конф. — Астана, 2008. — С. 106–109.

2   *Шаршеев К.* Новые оптические материалы на основе монокристаллов сложных соединений щелочных металлов: монография. — Каракол: Полиграф. ЫГУ им. К.Тыныстанова. — 2010. — 256 с.

3   *Radhakrishna S., Pande K.P.* Optical and electrical properties of some sulfates doped with cobalt // Phys. Chem. Sol. — 1972. — Vol. 34. — No. 8. — P. 2037–2044.

4   *Koketai T.A., Tagayeva B.S., Tussupbekova A.K., Mussenova E.K.* The effect of pre-irradiation defects on the recombination luminescence in activated crystals K2SO4 // Book of abstracts. International conference of luminescence and optical spectroscopy of condensed matter. — Wroclaw, Poland — 2014. — P. 39.

5   *Кукетаев Т.А., Ким Л.М., Махметов Т.С.* Рекомбинационная люминесценция в K_2SO_4-Cu^{2+} // Твердотельные детекторы ионизирующих излучений: Тезисы докладов междунар. конф. — Екатеринбург, 1997. — С. 113.

6   *Көкетай Т.Ә., Тусупбекова А.К., Мусенова Э.К., Ибраева А.Д., Сайдрахимов Н.Б.* Исследование закономерностей влияния ионов переходных металлов на радиационно-стимулированные процессы в сульфатах и фосфатах калия // Бейсызықты жүйелердегі хаос және құрылымдар. Теория және тәжірибе: 9 Халықарал. ғыл. конф. материалдары. — Қарағанды, 2015. — С. 499–502.

7   *Новосад С.С.* Спектральные и сцинтилляционные характеристики составных детекторов рентгеновского излучения, полученных на основе кристаллов иодистого кальция // Журнал техн. физики. — 1998. — Т. 68 (9). — С. 71–73.

8   *Baltabekov A.S., Koketaitegi T.A., Kim L.M.* The influence of impurity ions of transition metals on radiation induced prosseces // Eurasian Physical Technical Journal. — 2010. — Vol. 7. — No. 1 (13). — P. 12–17.

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Өтпелі металдар иондарымен белсендірілген калий сульфаты кристалдарында қоспа радиациялық ақауларын зерттеу

Мақалада өтпелі металл иондарымен белсендірілген калий сульфат кристалдарындағы қоспалы радиациялық ақаулар зерттелді. K_2SO_4-Co^{2+}, K_2SO_4-Mn^{2+}, K_2SO_4-Ni^{2+} кристалдарының зерттелінетін оптикалық жұту спектрлері бойынша объектілердегі нүктелік ақаулар мен қоспалар бойынша сапалық қорытындыларды жасауға болады. Рентген кванттарымен сәулелендіргеннен кейін кристалдардың қоспалық жұту жолақтарындағы оптикалық тығыздық төмендейді. Бұл құбылыс эквивалентті металл иондарының бастапқы иондарының зарядтық күйінің өзгерісімен түсіндіріледі және қоспа иондары не иондалады немесе электрондар үшін қармағыштар болады. Өтпелі Me^{2+} металл қоспа иондары калий сульфатында электрондарды қармау орталықтары болатыны анықталды.

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Исследование примесных радиационных дефектов в кристаллах сульфата калия, активированных ионами переходных металлов

В работе проведено исследование радиационных примесных дефектов в кристаллах сульфата калия, активированных ионами переходных металлов. По исследуемым спектрам оптического поглощения кристаллов K_2SO_4-Co^{2+}, K_2SO_4-Mn^{2+}, K_2SO_4: Ni^{2+} удается сделать качественные выводы о примесях и точечных дефектах в объектах. Отмечено, что после облучения рентгеновскими квантами оптическая плотность в примесных полосах поглощения кристаллов уменьшается. Это явление объясняется тем, что происходит изменение зарядового состояния у исходных ионов двухвалентных ионов металла, и примесные ионы либо ионизуются, либо являются ловушками для электронов. Выявлено, что примесные ионы переходных металлов Me^{2+} являются центрами захвата электронов в сульфате калия.

References

1   Kim L.M., Kuketaev T.A., Musenova E.K, Tagaeva B.S. *Chaos and structure in nonlinear sistems.* Theory and experiment: Material of second international Conf., Astana, 2008, p. 106–109.

2   Sharsheev K. *New optical materials based on single crystals of the complex compounds of alkali metals*, Monografiya, Karakol: Poligraf. YGU them. K.Tynystanova, 2010, 256 p.

3   Radhakrishna S., Pande K.P. *Phys. Chem. Sol.*, 1972, 34, 8, p. 2037–2044.

4   Koketai T.A., Tagayeva B.S., Tussupbekova A.K., Mussenova E.K. *Book of abstracts. International conference of luminescence and optical spectroscopy of condensed matter*, Wroclaw, Poland, 2014, p. 39.

5   Kuketayev T.A., Kim L.M., Makhmetov T.C. *Solid-state detectors of the ionizing radiation: International conference*, Yekaterinburg, 1997, p. 113.

6   Koketai T.A., Tussupbekova A.K., Mussenova E.K., Ibraeva A.D., Saydrakhimov N.B. *Chaos and structure in nonlinear sistems. Theory and experiment:* Material of 9th international Conf.: International Scientific Conference, Karaganda, 2015, p. 499–502.

7   Novossad S.S. *Technical Physics*, 1998, 68, 9, p. 71–73.

8   Baltabekov A.S., Koketaitegi T.A., Kim L.M. *Eurasian Physical Technical Journal*, 2010, 7, 1 (13), p. 12–17.