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Formation of a combined electron-hole emission state in the LiRbSO4 – Eu phosphor

In the irradiated phosphor $LiRbSO_4 - Eu$, the mechanisms of formation of the induced or combined electron-emitting state at 3.1-2.94 eV were studied using optical and thermal activation spectroscopy methods. It has been shown experimentally that the combined electron-emitting state of the phosphor is formed from the electron states of impurity and intrinsic electron and hole trapping centers of $Eu^{2+} - SO_4^-$ and $SO_4^{3-} - SO_4^-$. Electron and hole trapping centers are created by irradiating the phosphor with photons exceeding the width of the forbidden band of the matrix, where free electrons are created in the conduction band and a hole in the valence band. The trapping center is formed by the capture of free electrons by impurities and anionic complexes according to the reaction $Eu^{3+} + e^- \rightarrow Eu^{2+}$, $SO_4^{-2} + e^- \rightarrow SO_4^{3-}$. In one process with electron centers, holes in the form of SO_4^{2-} are localized. Thus, impurity and intrinsic $Eu^{2+} - SO_4^-$ and $SO_4^{3-} - SO_4^-$ electron-hole trapping centers are formed. Similarly, trapping centers are formed as a result of charge transfer from the excited anion of the SO_4^{2-} complex to the Eu^{3+} impurities and to the neighboring SO_4^{2-} anions according to the reaction ($O^{2-} - Eu^{3+}$) and ($O^{2-} - SO_4^{2-}$), and localized holes are also formed in one act along with it. Combined electron-emitting states consisting of impurity and intrinsic electron states are excited by photons with energies of ~4.0 eV and ~4.5 eV.

Keywords: electron; hole; recombination emission; intrinsic emission; sulfate; excitation.

Introduction

LiRbSO4 – Eu phosphors, like other sulfates, can be used in dosimetry, as can CaSO4 – Dy and CaSO4 – Eu. In phosphors activated by impurities, the Eu ion in the matrix may exist in different valences. For example, in CaSO4 – Eu impurities can be in the divalent state Eu^{2+} with an internally centered emission of about 390 nm. If Eu is in the trivalent state of Eu^{3+} in this matrix, emission is observed at 595–610 nm.

The luminescent properties of activated phosphors with an impurity of Eu have been studied for several decades [1–8]. In the works of the authors [9], redox reactions between $Eu^{2+} \leftrightarrow Eu^{3+}$ ions in CaSO4 – Eu were investigated. During thermal annealing up to 975 K and irradiation with gamma rays, based on measurements of photoluminescence, thermoluminescence, and EPR signal, the conversion of Eu^{2+}, ions to Eu^{3+}, as well as reverse reduction to Eu^{2+}, is demonstrated in phosphors.

In the work of the authors [10], a red glow was detected in a single crystal of sodium oxosulfate and yttrium NaY(SO4)2·H2O activated with Eu^{3+} to illuminate emitting displays.

In a review article by the authors [11], the luminescence of Eu^{3+} in various molybdates is considered. It was found that the emission at 615 nm corresponds to the 5D0–7F2 transitions in La2Mo2O9 – Eu^{3+} molybdenum.

In the work [12], authors detected red emission at 617 nm, which is excited in La2Zr3Mo2O9 – Eu^{3+} molybdates by Zr^{4+} and Mo^{6+} sensitizers at photon energies of 395.5 nm and 465 nm, respectively. These sensitizers are formed as a result of charge transfer from the matrix to the sensitizer ions, such as $O^{2-} – Zr^{4+}$ and $O^{2-} – Mo^{6+}$.

The mechanisms of formation of electron-hole trapping centers in sulfates of alkaline and alkaline earth metals activated by Mn^{2+}, Cu^+ and Dy^{3+} impurities were studied in the works of the authors [13–21]. It is shown that induced or combined electron-emitting states are formed in sulfates, which are excited in the transparency regions of the matrix at photon energies of approximately 4.0 eV and 4.5 eV.

A brief review of the literature shows that phosphors activated by Eu^{3+} ions emit photons in the red region of the spectrum. These intracenter emissions are mainly excited by sensitizers, which themselves are excited by the intrinsic electronic excitations of the matrix.

In this paper, the nature of the intracenter emission of the Eu^{3+} ion in the $LiRbSO_4$ matrix will be investigated, as well as the mechanism of formation of an induced or combined electronic emission state, which is formed from the electronic states of its intrinsic and impurity trapping centers when irradiated with photons exceeding the band gap.

Experimental part

The studied samples were synthesized by slow evaporation. To prepare the sample, 1.2 g of $LiRbSO_4$ powder and 0.3 mol% (0.37 g) Eu_2O_3 were used as starting materials.

Li_2SO_4 and Rb_2SO_4 (SigmaAldrich) were dissolved in double deionized water at a temperature between 35 and 40 °C. After ensuring the solution was transparent, each lanthanide was added and mixed one by one, checking the transparency of the solution. In a separate container, Eu_2O_3 was dissolved in a deionized solution of 40 ml at a temperature of 35–40 °C. Then both solutions were mixed at 35–40 °C within 1 hour. The solution was slowly heated, $LiRbSO_4$ (Sigma-Aldrich) powder was added and dissolved with stirring.

For luminescent measurements, a $LiRbSO_4$ sample doped with Eu^{3+} (0.3 mol.%) was obtained by adding Eu_2O_3 (Thermo Scientific, 99.99 %) to the process. $LiRbSO_4$ – Eu^{3+} was prepared by drying the doped sample at 550 °C in air. The finished powders were pressed into tablets with a size of 8–9 mm and a thickness of 1–2 mm. It was found that the optimal concentration of the Eu impurity in the $LiRbSO_4$ matrix is 0.3 mol.%. The resulting Eu impurity concentration of 0.3 mol.% was found to be optimal for spectroscopic properties in research.

Emission and excitation spectra were obtained using a spectrofluorimeter CM2203 (Belarus). The Solar CM2203 spectrofluorometer was used to measure the emission spectra in the spectral range of 1.5-6.2 eV.

Chemical analysis (EDX) was carried out on a TESCAN VEGA 3 LMH scanning electron microscope with an Oxford Instruments (UK) microanalyzer system. The resolution was 3 nm at 30 kV (SE), 6 nm at 30 kV (BSE), the magnification ranged from 6× to 300000×, and the screening magnification ranged from 12× to 600000×.

The thermally stimulated luminescence (TSL) method is one of the main experimental methods for studying trapping centers in dielectrics. To obtain TSL curves, the crystal under study is cooled to the boiling point of liquid nitrogen, 77 K. Under these conditions, the crystal is excited for some time by UV emission or X-ray emission. After the excitation stops, the crystal heats up at a constant rate of 0.2 deg/s, and the intensity of thermoluminescent emission is measured depending on the temperature.

Results

The nature of the intracenter emission of the Eu^{3+} impurity and new Raman emissions resulting from the interaction of impurities with the electronic excitations of the matrix were investigated.

The SEM figure (Fig. 1) shows that the powders have different sizes, approximately ranging from 5 to 200 microns (Fig. 1*a*). According to the results of SEM-EDX, a large number of peaks characteristic of metal ions were registered (Fig. 1*b*), confirming the presence of Eu content in the $LiRbSO_4$ powder.

a)   b)
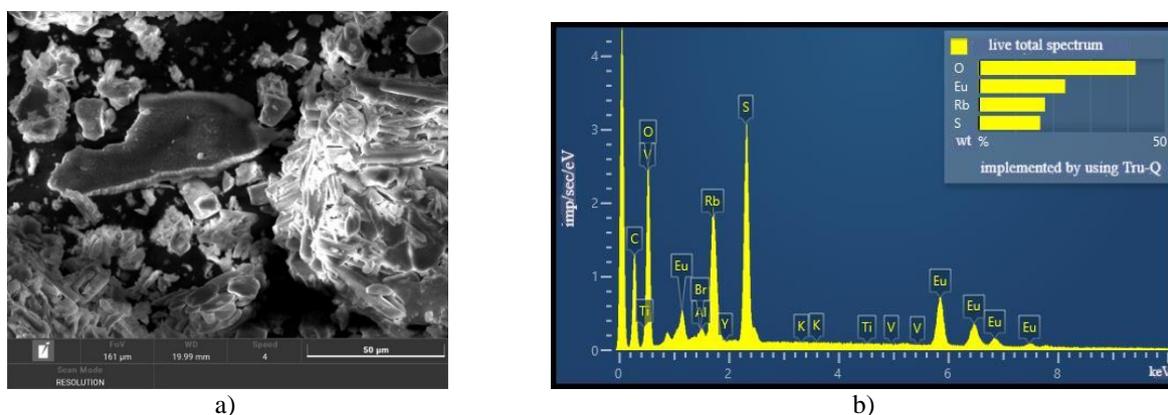
Figure 1. The result of SEM-EDX powder $LiRbSO_4$ – Eu

Figure 2 shows the emission spectrum of the $LiRbSO_4$ – Eu phosphor irradiated with photons with an energy of 5.46 eV at 300 K (curve 1). It can be observed from the figure that intracenter emissions of the

Eu^{3+} impurity appear at 2.03 eV, 1.9 eV, 1.8 eV, and 1.7 eV. The same phosphor was irradiated at 80 K (curve 2). Figure 1 shows that at 80 K, in addition to intracenter emission, new radiation bands appear at 3.1 eV, 3.0 eV, 2.9 eV, 2.6 eV, 2.4 eV, 2.3 eV, and 2.2 eV.
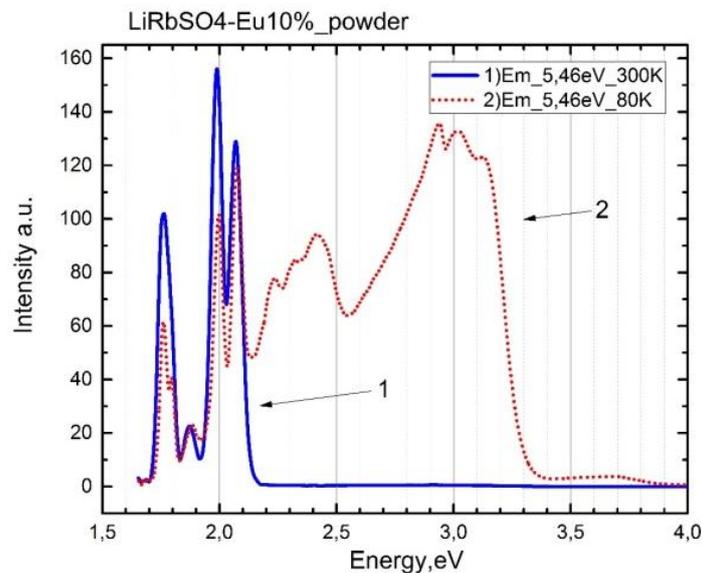
Figure 2. The emission spectrum of the $LiRbSO_4$ – Eu crystal at 300 K and 80 K:
when excited by photons: 1) $E = 5.46$ eV; 2) $E = 5.46$ eV

Figure 3 shows the excitation spectrum of new electronic radiative states at 3.1 eV, 3.02 eV, 3.4 eV, 2.94 eV, 2.43 eV, 2.32 eV, and 2.23 eV at 300 K and 80 K. It can be seen from the figure that at 300 K, the excitation bands are not clearly distinguished, and at 80 K, the excitation bands appear for emission of 2.94 eV, 3.02 eV, 3.1 eV, 3.92 eV, 4.43 eV, 5.64 eV, 5.9 eV, and 6.2 eV. From Figure 3 (curves 1–5), it can be seen that the newly formed emission states located in two spectral ranges, 3.1–2.94 eV and 2.43–2.23 eV, are mainly excited in three spectral regions of matrix transparency, 4.43–4.5 eV and 3.9–4.0 eV. Additionally, the same emission states related to trapping centers are created near the fundamental region at 5.64–6.2 eV as a result of charge transfer from anion to impurities or when an electron is captured by impurities or neighboring anions.
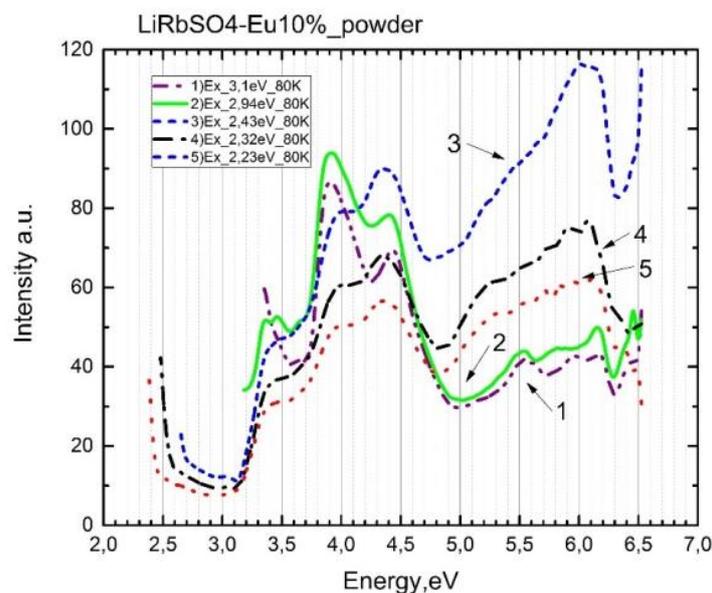
Figure 3. The excitation spectrum of the $LiRbSO_4$ – Eu crystal at 80 K: when excited by photons:
1) $E = 3.1$ eV; 2) $E = 2.94$ eV; 3) $E = 2.43$ eV; 4) $E = 2.32$ eV; 2) $E = 2.23$ eV

Figure 4 shows the excitation spectrum of a pre-irradiated phosphor at 300 K and 80 K for the bands 2.06 eV, 1.9 eV, 1.8 eV, and 1.7 eV of intracenter emission. From Figure 4 (curves 1, 2, 3, 4, and 1', 2', 3', 4'), it can be seen that excitation bands appear corresponding to the emission of Eu^{2+} ions in the $LiRbSO_4$ – Eu phosphor. The emission bands of the Eu^{2+} ion are excited by the emission of the Eu^{3+} ion in the red region of the spectrum.
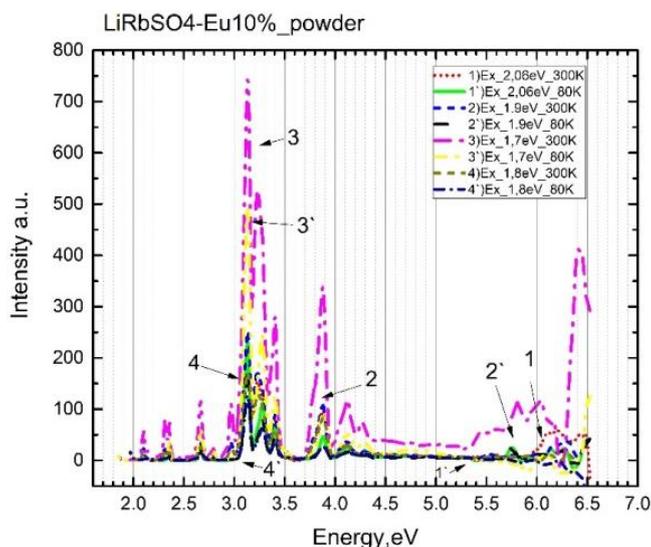
Figure 4. The excitation spectrum of the $LiRbSO_4$ – Eu crystal at 300 K and 80 K: when excited by photons:
1) $E = 2.06$ eV; 1') $E = 2.06$ eV; 2) $E = 1.9$ eV; 2') $E = 1.9$ eV; 3) $E = 1.7$ eV; 3') $E = 1.7$ eV; 4) $E = 1.8$ eV; 4') $E = 1.8$ eV

Figure 5 shows the emission spectra of a pre-irradiated phosphor excited in the transparency region of the matrix by photons with energies of 4.43-4.5 eV and 4.0 eV at 300 K and at 80 K.
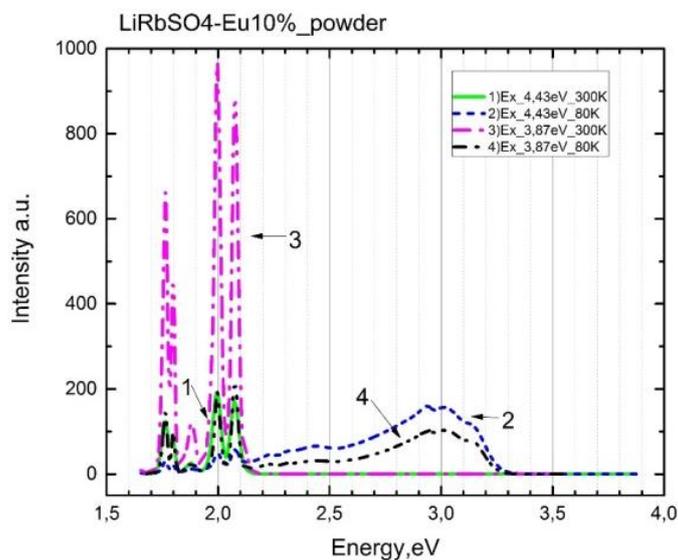
Figure 5. The emission spectrum of the $LiRbSO_4$ – Eu crystal when excited by photons:
1) $E = 4.43$ eV at 300 K; 2) $E = 4.43$ eV at 80K; 3) $E = 3.87$ eV at 300 K; 4) $E = 3.87$ eV at 80 K

Figure 5 (curves 1, 3) shows that when excited by photons with energies of 4.43-4.5 eV and 3.87-4.0 eV at a temperature of 300 K, intracenter emissions appear at 2.06 eV, 1.9 eV, 1.8 eV and 1.7 eV (curves 1 and 3). At a liquid nitrogen temperature of 80 K (curves 2 and 4), the intensity of the intracenter emission decreases 4-5 times, the positions of the bands are preserved. At 80 K, in addition to the intracenter emission, new radiation bands appear at 3.1 eV, 3.02 eV, 2.44 eV, 2.32 eV and 2.29 eV (curves 2, 4).

The measurement of the intensity of the intracenter and newly created emission radiation bands from the temperature of the matrix is shown in Figure 6.
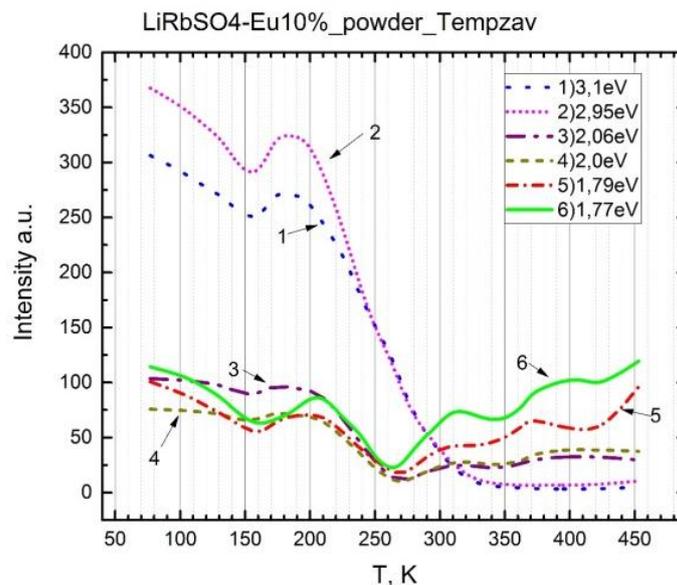
Figure 6. Temperature dependence LiRbSO$_4$ – Eu luminescence of radiation during excitation:
1) $E = 3.1$ eV; 2) $E = 2.95$ eV; 3) $E = 2.06$ eV; 4) $E = 2.0$ eV; 5) $E = 1.79$ eV; 1) $E = 1.77$ eV

It can be seen from the figure that the intensity of the new emission bands at 3.1 eV and 2.95 eV in the temperature range of 100–150 K gradually decreases and flares up at 150–200 K, then rapidly decreases to a minimum value in the range of 200–350 K (curves 1, 2). The temperature dependence of the change in the intensity of intracenter emission at 2.03 eV, 1.9 eV, 1.8 eV and 1.7 eV looks like this: in the temperature range from 100 K to 250 K, the intensity of all intracenter emission decreases rapidly, with some flare-up in the temperature range of 150–200 K, then in the temperature range of 280–450 K it rapidly increases to the maximum value.

Discussion

The novelty of the work is associated with the appearance of new emission bands when irradiated with photons in the fundamental region of the spectrum at 80 K, where free electron-hole pairs are created or as a result of charge transfer from the excited anionic complex SO_4^{2-} to impurities or to neighboring anions. In the early works of the authors [17], it was known that in irradiated alkali metal sulfates, recombination emission at induced trapping centers occurred in the spectral range of 3.0–3.1 eV, 2.6–2.7 eV, and 2.3–2.4 eV. Figure 5 (curve 2, 4) shows that at 80 K, the intensity of the intracenter emission band at 2.06 eV, 1.9 eV, 1.8 eV, and 1.7 eV decreased and new recombination emission appeared at 2.94–3.1 eV, which are excited at photon energies 3.92–4.0 eV and 4.43–4.5 eV. Low-energy recombination emission at 2.23–2.43 eV is also excited in this spectral region. These recombination emissions are generated in the fundamental spectral range of 5.64 eV, 5.9 eV, and 6.2 eV.

Thus, two groups of new recombination emissions at 2.94–3.1 eV and 2.23–2.43 eV are excited by photons with energies of ~4.0 eV and ~4.5 eV in the transparency region of the LiRbSO$_4$ – Eu phosphor. These photon energies at ~4.5 eV and ~4.0 eV are the absorption and excitation spectra of the electron-hole trapping center formed in the transparency region.

In the next stage, an irradiated phosphor with induced trapping centers was excited with a photon energy equal to the excitation spectrum of the trapping centers at ~4.0 eV and ~4.5 eV. At the same time, new recombination emissions appear back at 2.94–3.1 eV and 2.23–2.4 eV. The most important thing is that intracenter emissions of the Eu^{3+} impurity appear. These results mean that both emission, recombination, and intracenter radiative decay identically from an induced or combined electron emissivity state. By measuring the temperature dependence of the decay of the induced or combined electronic state, it is shown that the in-

tensity of the recombination emission state at 2.94–3.1 eV in the temperature range from 100 K to 250 K decreases to a minimum value.

The intensity of the intracenter emission of the impurity increases to the maximum value at 2.06 eV, 1.9 eV, 1.8 eV, and 1.7 eV temperature range.

The decay and formation of an induced or recombined electronic emission state can be explained in this way:

During irradiation with photons from 5.64–6.2 eV, electronic trapping centers are created during the localization of free electrons or during charge transfer from the excited anionic complex SO_4^{2-} to impurities Eu^{3+} ($O^{2-} - Eu^{3+}$) electronic impurity trapping centers of Eu^{2+} are formed in addition to the holes of SO_4^{-} localized near the ground state of the Eu^{3+} admixture. Thus, the centers of electronic trapping of impurities $Eu^{2+} - SO_4^{2-}$ are created. Similarly, when electrons are trapped or as a result of charge transfer from the excited anion SO_4^{2-} ($O^{2-} - SO_4^{2-}$) to neighboring anions, their intrinsic electron trapping centers SO_4^{3-} are formed, complementary to the holes SO_4^{-}. This is how the correct trapping centers $SO_4^{3-} - SO_4^{-}$ are formed.

Combined or induced electron-emitting states at 2.94–3.1 eV are created from the electronic states Eu^{2+} and SO_4^{3-} under the conduction band with a certain ionization energy to the conduction band.

During heating of a phosphor with induced emission states in the temperature range of 100–250 K, ionization of the electronic trapping centers occurs $Eu^{2+} \rightarrow Eu^{3+} + e^{-}$, $SO_4^{3-} \rightarrow SO_4^{2-} + e^{-}$. The free electron recombines with the hole SO_4^{-} near the Eu^{3+} admixture; the energy released during recombination excites the impurity in the temperature range 250–450 K, in which we observe a rapid increase in the intensity of red emission from the Eu^{3+} impurity. In this way, energy is transferred from the excited matrix to the impurities.

Conclusions

1. In the irradiated $LiRbSO_4$ – Eu phosphor, new stimulated and combined radiative states were discovered at 3.1–2.94 eV, which are excited at photon energies of ~4.0 eV and ~4.5 eV in the matrix transparency region.

2. The emission states of 3.1–2.94 eV are created when the anion is excited by photons with an energy of 5.64 eV as a result of charge transfer from the SO_4^{2-} ion to the impurities Eu^{3+} and the neighboring ion by the reaction ($O^{2-} - Eu^{3+}$) and ($O^{2-} - SO_4^{2-}$).

3. Based on the measurement of the excitation spectra of recombination emission of 3.1–2.94 eV and impurity emission of 2.06 eV, 1.8 eV and 1.7 eV, it was shown that they are simultaneously excited at photon energies of ~4.0 eV and ~4.5 eV. These values are the excitation spectrum of a new induced electronic radiative state consisting of intrinsic and impurity electronic states of trapping centers.

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LiRbSO$_4$ – Eu люминофорындағы біріктірілген электронды-кемтік сәулелену күйінің түзілуі

LiRbSO$_4$–Eu сәулелендірілген люминофорда оптикалық және термоактивациялық спектроскопия әдістерімен 3,1–2,94 эВ индукцияланған немесе біріктірілген электронды сәулелену күйінің пайда болу механизмдері зерттелді. Люминофордың біріктірілген электронды сәулелену күйі қоспа және меншікті электронды және кемтікті қармау орталықтары, электрондық күйінен Eu^{2+} − SO$_4^-$ және SO$_4^{3-}$ − SO$_4^-$ түзілетіні эксперименталды түрде көрсетілген. Электронды және кемтікті қармау орталықтары люминофордың тыйым салынған аймақ ені энергиясынан асатын фотондармен сәулелендіру кезінде құрылады, мұнда өткізгіштік зонасында бос электрондар және валенттік аймақта кемтік пайда болады. Қармау орталығы бос электрондарды, қоспалармен және анионды комплекстер қармалған Eu^{3+} + e^- → Eu^{2+}, SO$_4^{2-}$ + e^- → SO$_4^{3-}$ реакциясы бойынша түзіледі. Бір процесте SO$_4^{2-}$ түріндегі кемтіктер электронды орталықтармен локализацияланады. Осылайша, қоспа және меншікті Eu^{2+} − SO$_4^-$ және SO$_4^{3-}$ − SO$_4^-$ электрондық кемтіктік қармау орталықтары пайда болады. Осыған ұқсас SO$_4^{2-}$ комплексінің қозған анионынан Eu^{3+} қоспаларға және реакцияға сәйкес көршілес SO$_4^-$ аниондарға зарядтың ауысуы нәтижесінде басып алу орталықтары (O^{2-} − Eu^{3+}) және (O^{2-} − SO$_4^{2-}$), сондай-ақ бір процесінде онымен бірге локализацияланған кемтіктер түзіледі. Қоспалар мен меншікті электрондық күйлерден тұратын біріккен электрон шығаратын күйлер энергиясы, ~4,0 эВ және ~4,5 эВ фотондарымен қоздырылады.

Кілт сөздер: электрон, кемтік, рекомбинациялық сәулелендіру, меншікті радиация, сульфат, қозу.

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Образование комбинированного электронно-дырочного излучательного состояния в люминофоре LiRbSO$_4$–Eu

В облученном люминофоре LiRbSO$_4$–Eu методами оптической и термоактивационной спектроскопии исследованы механизмы образования индуцированного или комбинированного электронно-излучательного состояния при 3,1–2,94 эВ. Экпериментально показано, что комбинированное электронно-излучательное состояние люминофора формируется из электронных состояний примесных и собственных электронно- и дырочных центров захватов $Eu^{2+} - SO_4^-$ и $SO_4^{3-} - SO_4^-$. Электронно- и дырочные центры захвата создаются при облучении люминофора фотонами, превышающими ширину запрещенной зоны матрицы, где создаются свободные электроны в зоне проводимости и дырка в валентной зоне. Центр захвата образуется при захвате свободных электронов примесями и анионными комплексами по реакции $Eu^{3+} + e^- \rightarrow Eu^{2+}$, $SO_4^{2-} + e^- \rightarrow SO_4^{3-}$. В одном акте с электронными центрами локализуются дырки в виде SO_4^{2-}. Таким образом, формируются примесные и собственные $Eu^{2+} - SO_4^-$ и $SO_4^{3-} - SO_4^-$ электронно-дырочные центры захватов. Аналогично центры захвата образуются в результате переноса заряда от возбужденного аниона комплекса SO_4^{2-} к примесям Eu^{3+} и к соседним анионам SO_4^{2-} по реакции ($O^{2-} - Eu^{3+}$) и ($O^{2-} - SO_4^{2-}$), также в одном акте вместе с ним формируются локализованные дырки. Комбинированные электронно-излучательные состояния, состоящие из примесных и собственных электронных состояний, возбуждаются фотонами с энергией ~4,0 и ~4,5 эВ.

Ключевые слова: электрон, дырка, рекомбинационное излучение, собственное излучение, сульфат, возбуждение.

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