Optical properties of Cu₂O nanowhiskers

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The optical properties of Cu₂O nanowhiskers grown by the liquid method with material deposition in an electric field have been studied. The spectral lines forbidden by the selection rules for perfect Cu₂O crystals were found in the Raman spectra. The nature of related phonon states is analyzed. In the photoluminescence spectra in the red and near-IR regions, broad bands of defective origin are observed. It was found that the presence of a band at 650 nm (1.9 eV) is a specific feature of the photoluminescence of nanowhiskers. Its properties are studied and possible radiation mechanisms are discussed. In the intrinsic absorption region of nanowhiskers, the photoluminescence band at 572 nm (2.17 eV) associated with band−band transitions is detected. At a low excitation level, the emission of a free exciton $n = 1$ of the yellow exciton series is observed with simultaneous emission of an optical phonon.

1. Introduction

Copper oxide (Cu₂O) is a model object for studying exciton states. Absorption and emission spectra of free excitons, exciton spectra with the participation of optical phonons, emission of bound and so-called relaxed excitons in the near IR region are observed in it [1–4].

On the other hand, Cu₂O has various technical applications. Copper oxide is used as a solar energy converter with 18% efficiency. In recent years, Cu₂O nanocrystals were used as photocatalysts on industrial scale to decompose water into hydrogen and oxygen [5,6].

In this paper we study the optical properties of nanowhiskers Cu₂O using photoluminescence (PL) and Raman scattering (RS) methods. The purpose of the paper is to study the structure of energy levels inherent in nanowhiskers obtained by the liquid method.

2. Experiment procedure

Cu₂O nanocrystals were obtained by a liquid method using the method of substance deposition in the electric field [7]. The samples were an array of whiskers with an average length of 2 μm and a diameter of 180 nm, located on a copper substrate (Fig. 1). The whiskers had a polycrystalline structure and retained the cubic modification [7]. For comparison with nanowhiskers we studied bulk crystals of Cu₂O, obtained by high-temperature oxidation of copper from a melted schicht by the UHF method, and natural mineral Cu₂O from Namibia.

The photoluminescence measurements were carried out in the temperature range from 5 to 300 K using a Janis

Research closed-cycle helium cryostat and an MDR-204-2 double monochromator (LOMO Photonica, St. Petersburg, Russia) with a dispersion of 25 Å/mm. The spectra were excited by lasers with wavelengths of 325, 454.6, and 532 nm.

Raman scattering studies of Cu₂O were carried out at room temperature. To measure unpolarized spectra in the „backscattering" geometry, we used a spectrometer LabRAM HREvo UV-VIS-NIR-Open (Horiba, Lille, France) equipped with a confocal microscope and a silicon CCD matrix cooled to liquid nitrogen temperature. The line $\lambda = 532$ nm (2.33 eV) of Nd:YAG laser (Torus, Laser Quantum, Inc., Edinburg, UK) was used to excite the Raman spectra. The lens Olympus 100× (NA = 0.9) was used to focus the laser beam on the sample surface into a spot ∼ 1 μm in diameter. The
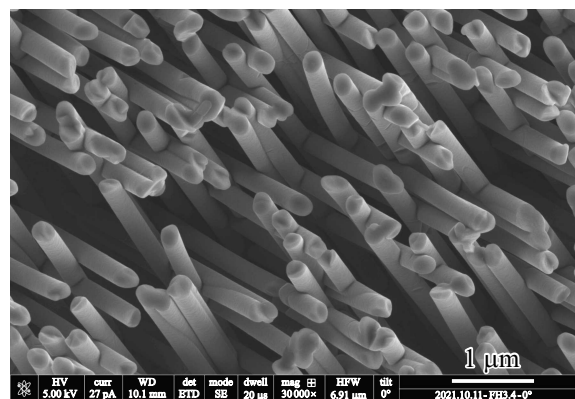
Figure 1. SEM image of the array of Cu₂O whiskers obtained by the liquid method.

spectra were recorded using diffraction gratings of 1800 and 600 grooves/mm.

3. Results and discussion

3.1. Raman scattering

Cu_2O crystallizes in a cubic lattice that belongs to the space group O_h^4, or $Pn3m$ (point symmetry O_h, or $m3m$). The unit cell Cu_2O contains two formula units (6 ions) and, therefore, there are 18 vibrational modes at the Γ point of the Brillouin zone. Three acoustic modes have T_{1u} symmetry. Among 15 optical modes two triple degenerate symmetry modes T_{1u} are active in the infrared (IR) spectrum, one triple degenerate mode T_{2g} is active in the Raman spectrum, and the remaining 6 modes are silent [8]. Thus, in the Raman spectrum of the first order Cu_2O, only one line allowed by the selection rules should be observed.

Fig. 2 shows the Raman spectra obtained at room temperature from an array of Cu_2O whiskers (curve *1*) and from a high-quality single crystal Cu_2O (mineral from Namibia) (curve *2*). Similar spectra from single crystals were presented in a large number of papers related to the study of the dynamics of the crystal lattice of structurally perfect single crystals and Cu_2O films [9]. It can be seen that in the spectrum a line at a frequency of $220\,cm^{-1}$ prevails, which is in strong contradiction with the position $550\,cm^{-1}$ for the mode allowed to be observed in the Raman spectrum Cu_2O, which was theoretically predicted [8]. It was shown for the first time in [10] that the line at frequency of $220\,cm^{-1}$ is actually an overtone of the mode $110\,cm^{-1}$ allowed for observation only in IR spectra. In the same paper, the dominant role of the peak at frequency of $220\,cm^{-1}$ in the Raman spectrum of Cu_2O single crystal was explained. For this purpose, the authors of the mentioned work analyzed the Carabatos and Prevot calculations of the phonon dispersion curves Cu_2O [11], which indicate that the special behavior of the dispersion curve of mode $110\,cm^{-1}$ should lead to the appearance of an intense narrow peak in the two-phonon density of states. In turn, a comparison of the Raman spectrum and the yellow series of exciton luminescence made it possible for authors of paper [10] to discover that the exciton-phonon interaction for phonon with frequency of $110\,cm^{-1}$ is much stronger than for some other phonon. This interaction causes a violation of the selection rules and, as a consequence, the dominance of the line at frequency of $220\,cm^{-1}$ in the spectrum of a perfect single crystal Cu_2O. It was also shown in paper [10] that the line allowed by the selection rules in the Raman spectrum of Cu_2O, which is not observed at room temperature, appears at frequency of $515\,cm^{-1}$ in the spectrum measured at $T = 4\,K$.

As it was shown in a number of papers (see, for example, [12,13]), the violation of the selection rules in the Raman spectra of Cu_2O occurs not only due to the strong
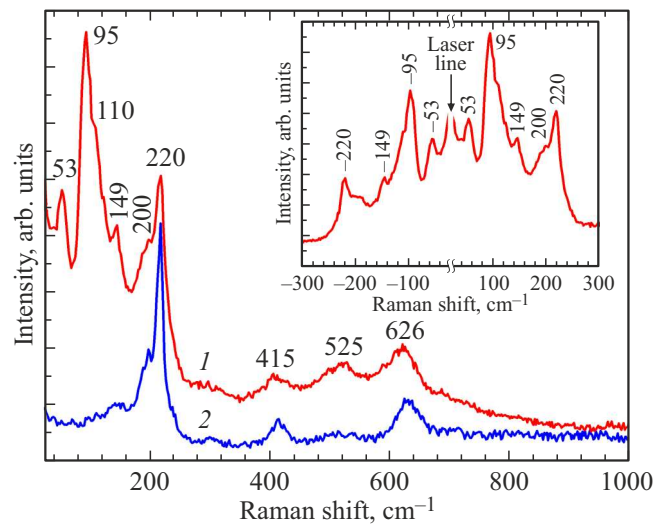
Figure 2. Raman spectra of array of Cu_2O whiskers (curve *1*) and single crystal Cu_2O (curve *2*) for $T = 300\,K$. Insert — low-frequency Raman spectrum of nanowhiskers in the Stokes and anti-Stokes regions.

exciton-phonon interaction near resonances, but also due to the presence of defects and nonstoichiometry of elemental composition. As a result, forbidden modes are observed in the Raman spectra of such samples. An example of this is the Raman spectrum of nanowhiskers shown in Fig. 2 (curve *1*). In this spectrum, in addition to the mode at frequency of $220\,cm^{-1}$, one can see additional modes at frequencies of 53, 95, 110, 149, 415 and $626\,cm^{-1}$, which refer to forbidden modes, their combinations, or overtones of high orders of Cu_2O. These modes arise in the Raman spectrum due to the violation of the rules for selecting phonons by the wave vector, which indicates the imperfection of the crystal structure of nanowhiskers. The phonon mode with lowest frequency in the Raman spectrum of Cu_2O nanowhiskers is at frequency of $53\,cm^{-1}$, which is confirmed by its observation in the anti-Stokes part of the Raman spectrum shown in the insert to Fig. 2. As far as we know, this is the first experimental discovery of this mode.

And at the end of this Section note the unusual behavior of the line at frequency of $525\,cm^{-1}$, which is close to the mode frequency allowed by the selection rules in the Raman spectrum of the Cu_2O single crystal. This line is not observed in the spectrum of the perfect crystal measured at room temperature, but is clearly visible in the spectrum of nanowhiskers (Fig. 2, curve *1*). A similar intensity increasing of this spectral feature was observed in defective Cu_2O single crystals [12,13]. The reason for the low intensity of the line at frequency of $525\,cm^{-1}$ in the Raman spectrum of ideal crystal Cu_2O and its increase with defectiveness increasing of the structure was not yet reliably explained. In the mode $T_{2g}\,(\sim 550\,cm^{-1})$ allowed to be observed in Raman spectra, only oxygen atoms oscillate. It can be supposed that the reason for its low intensity is a

consequence of compensation for the contributions of the longitudinal and transverse deformation polarizabilities of the Cu−O bonds in the structure with ideal tetrahedra.

3.2. Photoluminescence spectra

Fig. 3 shows the PL spectrum of an array of Cu_2O whiskers at 5 K. The spectrum consists of intense bands with maxima at ~ 650 and 720 nm, as well as weak broad bands with maxima at 570 and 810 nm. In all the studied samples PL maximum is also observed in the region 910−940 nm (not shown in the Figure). Note that the emission maximum at 570 nm is in the region of the yellow exciton series. At some points of the array at low excitation intensity one can also observe a narrow line at $\lambda = 614$ nm, which corresponds to the $n = 1$ state of the yellow exciton series with simultaneous emission of an optical phonon (see inset in Fig. 3). The exciton line disappears in the spectrum as the excitation intensity increases. This circumstance indicates that free excitons present in bulk can also exist in our samples. The short-wavelength band with maximum at 572 nm (2.17 eV) can be associated with band−band [14] transitions, and in the long-wavelength part of the maximum — with spectrally unresolved lines of the yellow exciton series.

The position of broad maxima can shift a little at different points of the sample (Fig. 3).

For comparison with nanowhiskers, we studied bulk crystals Cu_2O (Fig. 4). The sample insert space obtained by high-temperature oxidation of copper, the sample *2* — was grown from the melted schicht by the microwave method, the sample *3* — is a mineral from Namibia. Sample *3* is considered the most perfect: its exciton absorption and luminescence spectra [15] contain the largest number of exciton lines. The large variability of the broad bands spectra indicates their defective origin. As can be seen from the Figures, no band at 650 nm is observed in all the investigated bulk samples. Generally this band is rarely observed in the spectrum of bulk samples Cu_2O. The nature of broad bands in bulk was studied many times [4,16–18]. The radiation in them was associated with different options of the transitions conduction band−defect and defect−-valence band. In the paper [4] the emission of the ~ 700 and 900 nm bands was associated with the emission of excitons relaxed on defect states.

Much less data is available about the band with $\lambda = 650$ nm. In the paper [3] the authors observed the structure of this band and associated it with the process exciton−exciton interaction. Note that such a process is possible at a high density of excitons. In the paper [16] it is assumed that this line occurs at the transition conduction band−defect.

The spectral position of the broad bands in the emission of nanowhiskers can differ somewhat at different points of the array (Fig. 3). The intensity ratio of the bands can also change, but number of bands remains constant.
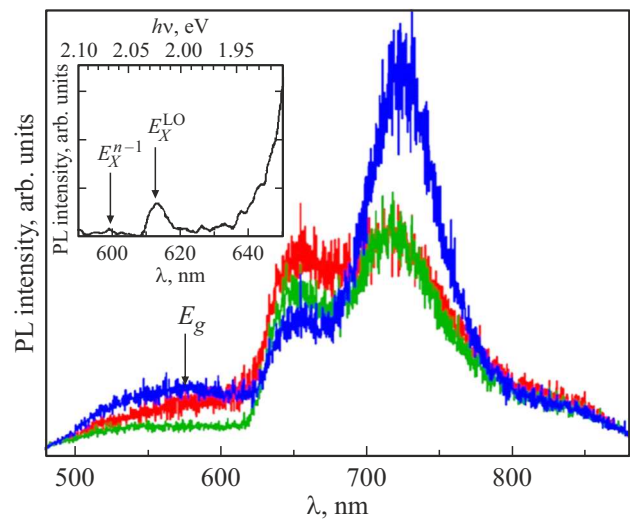

Figure 3. PL spectra of array of Cu_2O whiskers at $T = 5$ K at different points of the sample. In the insert — PL of the spectral region $n = 1$ of the yellow exciton series Cu_2O. (Colored version of the figure is presented in electronic version of the article).

Fig. 5 shows the change in the PL spectrum of nanowhiskers with the excitation intensity increasing. In the initial state, at a low excitation level, the 650 and 720 nm bands have approximately equal intensity, but as the intensity of the exciting laser increases, the 720 nm band becomes predominant in the spectrum. Note also the shift of the 650 nm band towards the short wavelength. It can be seen from the Figure that the rate of intensity increasing with excitation amplification for the 720 nm band is greater than for the 650 nm band.

It was found that the PL spectrum of array of nanowhiskers depends not only on the excitation intensity, but also on the exciting laser energy. Fig. 6 shows the PL spectra of whiskers obtained using lasers with different generation wavelengths. When PL is initially excited by a green laser ($\lambda = 532$ nm), only one band in the region of 650 nm is usually observed in the sample radiation (Fig. 6, *a*, curve *1*). Upon subsequent excitation of the same point of the whiskers array by a laser with $\lambda = 434$ nm, mainly 720 nm band appears in the radiation (Fig. 6, *a*, curve *2*). And finally, the curve *3* in Fig. 6, *a* demonstrates (third measuring) the PL of the same region of the sample when excited by the green laser ($\lambda = 532$ nm) — in this case, both bands 650 and 720 nm are simultaneously present in the emission spectrum.

The described emission pattern is mainly observed over the entire surface of the sample, however, at some points in the initial PL spectrum, the 720 nm band is already present upon primary excitation by a green laser (Fig. 6 *b*, curve *1*), and subsequent illumination of this region with 434 nm laser (Fig. 6, *b*, curve *2*) leads only to a relative enhancement of the 720 nm band (compare with curve *2* in Fig. 6, *a*).

Note that the use of „blue" laser in the studied samples always leads to a change in the ratio of the PL bands, the
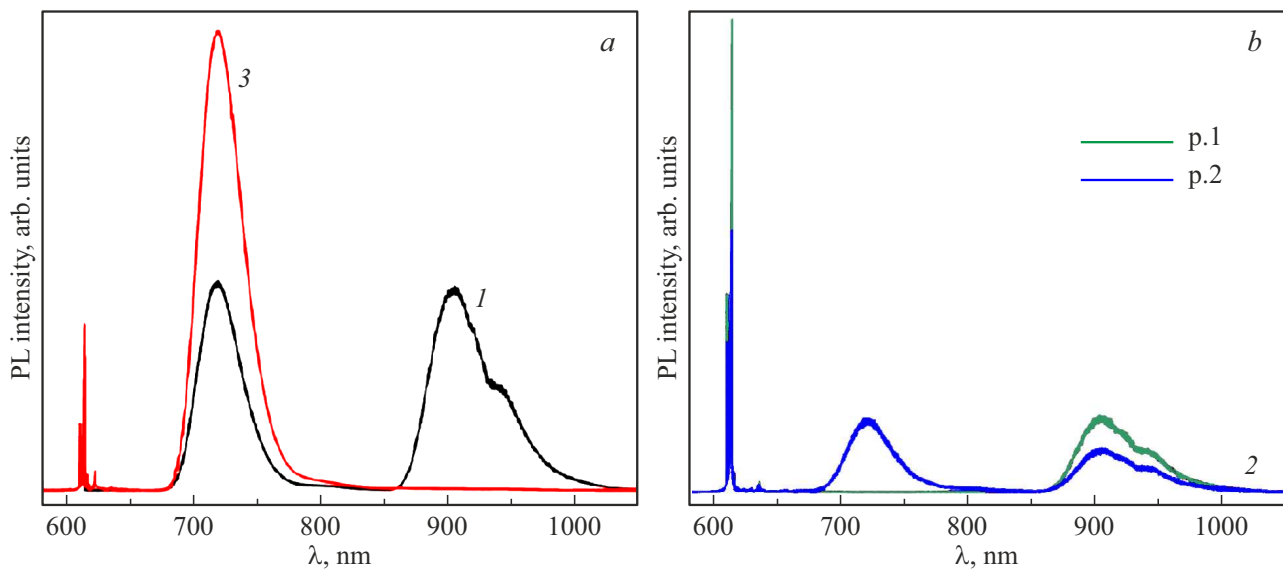
Figure 4. PL spectra of Cu_2O crystals obtained by various methods: *1* — high-temperature copper oxidation; *2* — from the charge melt by the microwave method (the spectra are shown at different points); *3* — natural mineral from Namibia. (Colored version of the figure is presented in electronic version of the article).
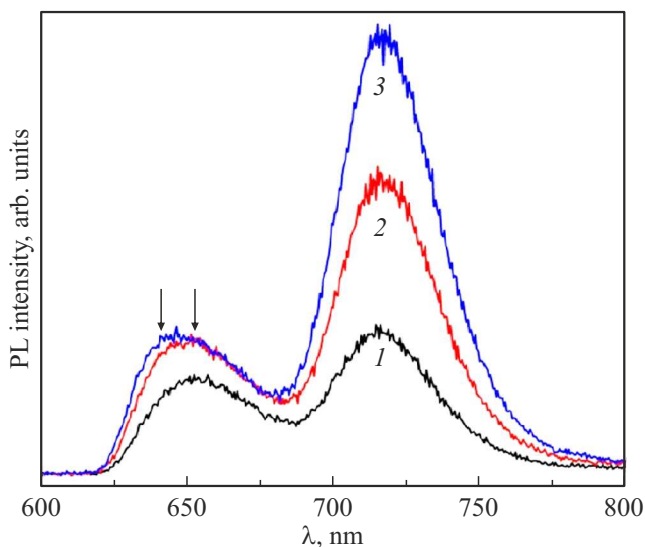
Figure 5. PL spectra of array of Cu_2O ($T = 5\,K$) whiskers at different laser excitation power, mW: *1* — 10, *2* — 40, *3* — 60.

intensity of the 650 nm band decreases significantly, and the band with maximum 720 nm becomes predominant in the radiation.

Further, when discussing the nature of these bands, one should take into account the relative intensities of the lasers used and the effect of possible heating of the samples at high excitation intensity.

When analyzing the PL of nanowhiskers, an important fact is the presence of the 650 nm band at the lowest excitation levels, which speaks against its belonging to exciton-exciton interaction processes.

In bulk crystals, in the described spectral region, only 720 nm emission band and a series of narrow bands in the 610−635 nm region, which belong to the exciton yellow series radiation, are observed. The PL spectra hardly change spectrally upon excitation by any of the lasers we used.

As the temperature insert space PL bands: 650 and 720 nm weaken in intensity and shift towards longer wavelengths (Fig. 7, *a*). The 720 nm band is observed in the PL spectra up to 180 K, while the 650 nm emission disappears already at $T = 80\,K$. In this case, the intensity of the short-wavelength part of the 650 nm band decreases more rapidly. As the temperature rises, the band becomes more symmetrical. The analysis of the PL spectra of the studied samples of nanowhiskers at different temperatures suggests a complex nature of the 650 nm band emission. Fig. 7, *b* shows the result of decomposition of the PL spectrum for $T = 5\,K$. It can be seen that the 650 nm radiation consists of two bands with maxima at 635 and 657 nm. The insert in Fig. 7, *b* shows the temperature dependences of all three PL bands obtained from the decomposition of the spectra. It can be seen that the short-wavelength part of the 650 nm band disappears already at $T = 60\,K$, while the long-wavelength part is observed in the spectrum up to $T = 80\,K$.

The complex nature of the 650 nm emission band is possibly also responsible for the nature of the PL transformation with pump power increasing (Fig. 5). Maybe the short-wavelength shift of the 650 nm band observed by us is associated with the redistribution of the 635 and 657 nm components described above, i.e. as the pumping is increased, the short-wavelength component grows faster.

Thus, PL spectra of the studied nanowhiskers exhibit a rich structure in the red and near-IR spectral regions.
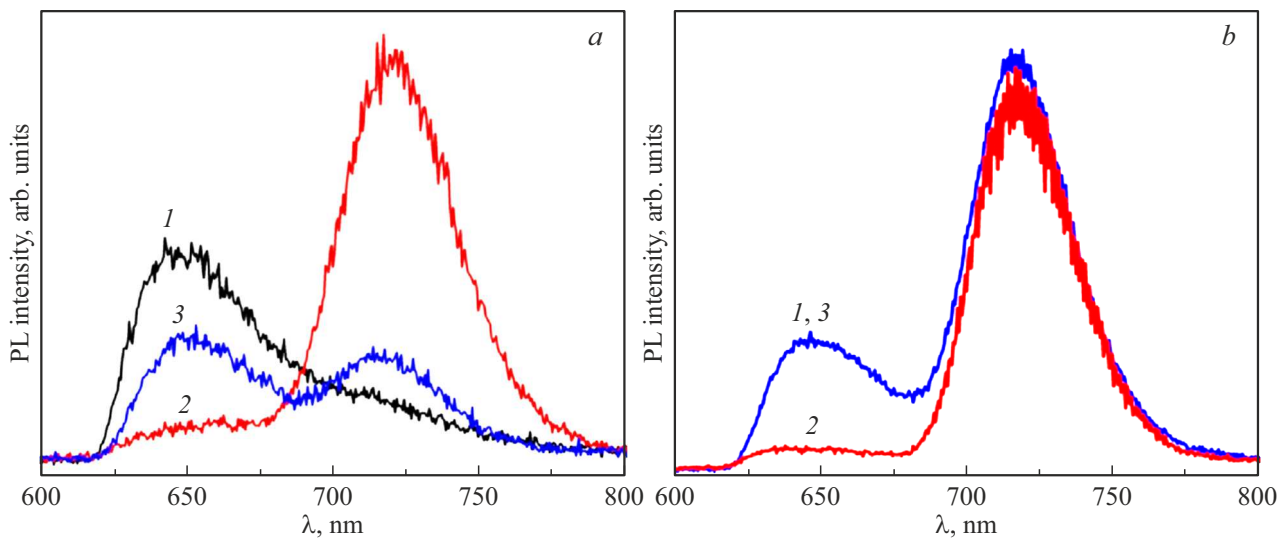
Figure 6. PL spectra of whiskers obtained at different points of the sample (*a*) and (*b*) using lasers with different generation wavelengths: *1, 3* — PL excitation by laser with $\lambda = 532$ nm, *2* — $\lambda = 434$ nm.
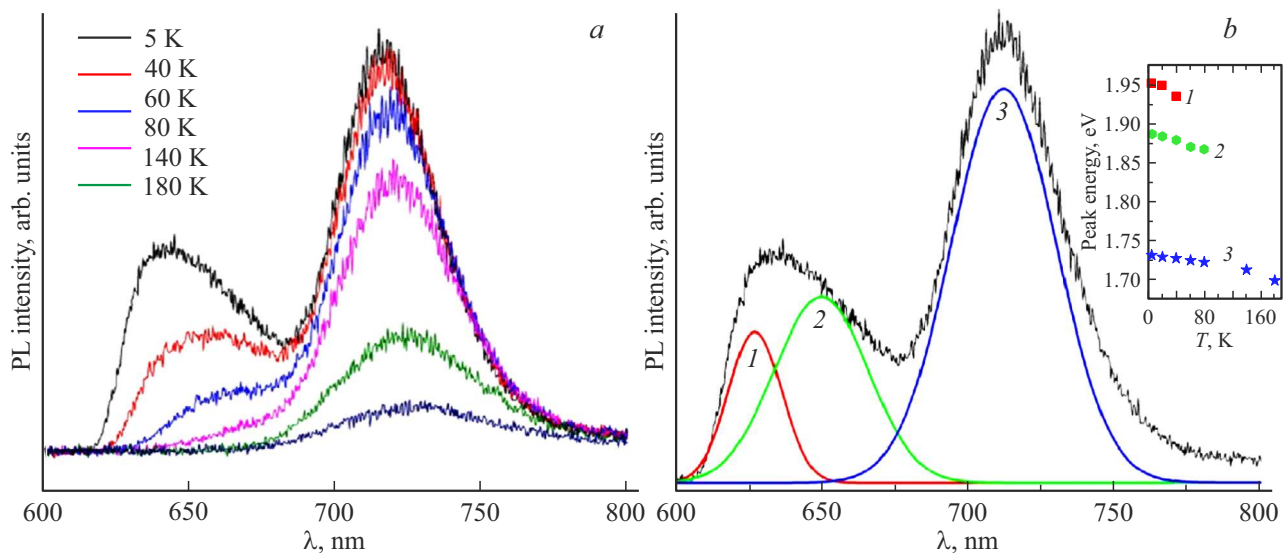
Figure 7. *a* — PL spectra of array of Cu₂O whiskers as function of temperature ($T = 5-180$ K). *b* — the result of expansion of the Cu₂O PL spectrum at $T = 5$ K. On the insert — the intensity of the PL maxima vs/ temperature for the bands: 535 (*1*), 657 (*2*) and 720 nm (*3*).

In IR region, these are broad bands, some of which are also observed in bulk samples. A distinctive feature of nanowhiskers is the existence of the emission band at 650 nm, which is rarely observed in bulk crystals. The characteristic properties of this band are a shift towards the short-wavelength with excitation intensity increasing; selective excitation from the region close to the width of band-gap;; a clearly-defined, in contrast to the 720 nm band, temperature dependence, as well as its doublet structure.

We assume that the 650 nm band has a complex structure, including contributions from the exciton and the acceptor center. As was shown in the paper [19], the exciton can be localized in the space charge layer. This corresponds to the

discrete levels formation in the potential well. They can be somewhat broadened due to dissociation in electric fields and screening.

It can be preliminarily assumed that the 650 nm band is a manifestation of a surface exciton localized at acceptor centers. The presence of two maxima in the contour of the 650 nm band in this case corresponds to the levels of the surface exciton. With pumping increasing, a higher level increases; it first of all goes out with temperature increasing. The binding energy of the surface exciton will be determined by the depth of the potential well. As follows from the experiment, the maxima associated with it disappear in the spectrum even at temperature of 80 K.

The relatively rare observation of the 650 nm band should be associated with the state of the surface. It can be supposed that the 650 nm band will be sensitive to various types of surface impacts.

The PL bands 720 nm, as well as 910−940 nm, are attributed in the literature to the PL of excitons relaxed on defects. The nature of these bands in Cu_2O single crystals was studied many times [4,18].

Besides, a broad PL band with a maximum of ~ 570 nm is observed in the region of the yellow exciton series. According to the spectral position, the maximum of the band coincides with the energy of width of band gap Cu_2O and in the paper [14] is associated with the recombination of free carriers. The luminescence disappearance of free excitons can be associated both with their ionization in strong heterogeneous electric fields on the surface and in the bulk of the samples [20], and with Coulomb screening with carrier concentration increasing. The effect of Coulomb screening on the disappearance of exciton lines in CdSe crystals was observed in [21]. The predominance of screening effects in our experiments is more likely. The $n = 1$ line is observed in the spectrum of nanowhiskers only at low excitation intensities and disappears with pumping increasing.

4. Conclusion

The performed optical studies revealed important features in the Raman and PL spectra of Cu_2O nanowhiskers, obtained by the original liquid method — ignition of forbidden transitions in RS, screening of exciton states at high excitation density, occurrence of band−band transitions and observation in the PL spectra of 650 nm band.

It is shown that the presence of band 650 nm (1.9 eV) is a distinctive feature of the studied samples of nanowhiskers. The study of the properties of this radiation made it possible to suppose its relationship with the radiation of the surface exciton localized at the acceptor center.

The conclusion is made about the nature of the PL band at 572 nm (2.17 eV) in the intrinsic absorption region of nanowhiskers. It is supposed that it is associated with band−band transitions. It is found that, at a low excitation level, the emission of a free exciton $n = 1$ of the yellow exciton series is observed with simultaneous emission of an optical phonon.

Conflict of interest

The authors declare that they have no conflict of interest.

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