Combinational processes in uranyl structures

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Abstract. It is established that the photoluminescence spectra of uranyl compounds have a shape of combination bands as equidistant Stokes satellites. These satellites correspond to the transitions from the excited electronic state to the vibrational states of fully-symmetric mode with the frequency of 854 cm$^{-1}$. The stimulated Raman scattering of light in uranyl compounds is observed when excited by the ultra-short powerful pulses of the laser YAG: Nd$^{3+}$ ($\lambda$=532 nm). The detected combinational processes open the possibility for detecting the uranyl compounds in mixtures and in the environment. The article analyses the conditions for the realization of laser generation in the uranyl compounds.

1. Introduction

The registration of the uranyl compounds spectra is an important task for detecting these compounds in the environment and using them as the components for industrial purposes. In particular, it is of great interest to record the Raman-spectra (RS) of uranium structures containing the uranyl ion (UO$_2$)$^+$. In the vibrational spectra of such compounds there is a high-quality fully-symmetrical mode with the frequency of 854 cm$^{-1}$. The RS of analytes with the ion (UO$_2$)$^+$ relate to the corresponding combinational satellite. Accordingly, the RS can serve as a reliable indicator of the uranyl-ion. Previously the RS of compounds with the uranium dioxide powder were registered during the excitation by helium-neon laser with the power of about 10 mW and with the use of a double monochromator providing the 2 cm$^{-1}$ resolution [1].

In [2] the RS were measured for the polycrystalline minerals with the uranyl-ion, and in [3] the RS of uranylacetates dissolved in water were recorded. The RS of sodium uranyl acetate NaUO$_2$(CH$_3$COO)$_3$ solid crystal were registered upon excitation with the argon laser ($\lambda$=514 nm), photomultiplier and spectrograph [4] as well as in the excitation radiation by the xenon lamp [5,6]. Theoretical calculations of the crystals NaUO$_2$(CH$_3$COO)$_3$ vibrational spectrum were provided in [7].

In this paper we posed the problem of express detection of compounds with uranium dioxide (UO$_2$) based on the modern methods of express registration of such spectra as RS and photoluminescence (PL). These methods involve the use of a micro probe and a small-size high-power spectrometer with a multiple element secondary radiation receiver.
2. Experimental part

The Raman-spectra of uranyl compounds were recorded using the micro probe and the continuous laser with the generation wavelength $\lambda=785$ nm and the average power $P=300$ mW (see Figure 1). The samples for the study were the polycrystals of sodium uranyl acetate $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ and the uranium glass.

The laser radiation (6) passed by means of quartz fibers through the interference filter (5) and was focused with a collecting lens (4) on the surface of the investigated sample (1). The scattered radiation was incident on the photonic crystal (5). The filter passed the laser radiation with the wavelength $\lambda=785$ nm and reflected the long-wave radiation. The scattered radiation entered the spectrometer (8) and the lens (4). Then the scattered radiation was analyzed by means of the computer (9). The resolution of the spectra was 2 cm$^{-1}$.

The luminescence spectra were recorded using the FSD-10 spectrometer with the sensitivity range of 200-1100 nm. The complexes were optically excited with the wavelength of 385 nm (3.24 eV). We used a quasi-monochromatic semiconductor LED (see Figure 2). The semiconductor LED consisting of a mirror (1), an electron and hole layers (2 and 4), p-n junction (3) and a collecting lens (5) generated the quasi-monochromatic radiation with the wavelength of $\lambda=385$ nm. This radiation was directed to the surface of the sample (8) using a probe (6) and quartz fibers (7). The sample was fixed on the object table (9). The reflected or transmitted signal was directed to a digital minispectrometer FSD-10 (10) and then it was analyzed using a computer (11).

Figure 1. Experimental setup for the registration of Raman-spectra: 1 – sample, 2– substructure, 3 – object table, 4 – focusing lens, 5– probe, 6 – laser radiation, 7 – refractor, 8 – FSD-10 spectrometer, 9 – computer.
Figure 2. Experimental setup for the registration of uranyl-compounds PL: 1 – mirror, 2 и 4 – electron and hole layers, 3 – p-n junction, 5 – collecting lens, 6 – probe, 7 – quartz fibers, 8 – sample, 9 – object table, 10 – minispectrometer FSD-10, 11 – computer.

3. Results and discussions

The PL and Raman-spectra of sodium uranyl acetate NaUO$_2$(CH$_3$COO)$_3$ are shown in Figure 3. The PL spectrum of this crystal consisted of four equidistant (in frequency) lines with the 854 cm$^{-1}$ shift (see Figure 3a). There were 14 lines in the spontaneous RS-spectrum - more than in the results presented in the paper [7]. The values of the corresponding frequencies of the Raman lines as well as their classification according to the vibration types are given in Table 1. In this table we compare our results with the literature data [7-10].

The frequencies 854 cm$^{-1}$ (O-U-O), 956 cm$^{-1}$ (C-C) and 1479 cm$^{-1}$ (O-C-O) correspond to the valence type $A_1$ fully symmetric vibrations $\nu_s$ of the NaUO$_2$(CH$_3$COO)$_3$ crystal T point symmetry group. The frequency 931 cm$^{-1}$ corresponds to the antisymmetric mode $\nu_{as}$ (type E). The frequencies 222 and 255 cm$^{-1}$ (O-U-O), 676 and 689 cm$^{-1}$ (O-C-O) correspond to the deformation mode (F).

The most intense line in the Raman spectrum of the uranyl acetate sodium crystal with the frequency of 854 cm$^{-1}$ is also present in the Raman spectra obtained earlier for Cu[(UO$_2$)$_4$(SeO$_3$)$_2$O$_2$]-8H$_2$O [7] and CsUO$_2$(NO$_3$)$_3$ [8,9]. This line can be attributed to the fully symmetrical UO$_2$ oscillation [11]. Thus, in the Raman and PL spectra of the sodium uranyl acetate crystal a valence fully symmetrical vibration is manifested. This oscillation can be used for the uranyl compounds detection.
Figure 3. The PL spectra (a) and RS spectra (b) of polycrystalline sodium uranyl acetate NaUO$_2$(CH$_3$COO)$_3$. The semiconductor LED provided optical excitation of luminescence (curve 2) with the wavelength $\lambda=385$ nm (curve 1). The RS spectrum was carried out with the $\lambda=785$ nm CW laser excitation, and the acquisition time was 6 s.

The PL and Raman-spectra of the uranyl glass are shown in Figure 4. In the PL spectrum of the uranyl glass the phonon repeats with a spectral shift close to the frequency of the fully symmetric vibration of the uranyl group UO$_2$: 850 cm$^{-1}$. The photoluminescence spectrum shifts to the red region of the spectrum (see Figure 4 a) in comparison with NaUO$_2$(CH$_3$COO)$_3$. 
Table 1: Crystal NaUO$_2$(CH$_3$COO)$_3$ frequencies in the infrared absorption spectrum (IR) [9] and Raman – spectra. The frequencies in the Raman – spectra (RS) were obtained theoretically [6]. RS* – the results obtained in this paper.

| NaUO$_2$(CH$_3$COO)$_3$ | Corresponding Translational modes |
|-------------------------|----------------------------------|
| IR[9]                   | RS[6]   | RS*   |
| 470                     | 480     | 222   |
| 609                     | 610     | 255   |
| 675                     | 677     | 418   |
| 676                     | 685     | 480   |
| 826                     | 852     | 610   |
| 936                     | 931     | 677   |
| 950                     | 957     | 676   |
| 1005                    | 1057    | O-C-O |
| 1053                    | 1344    | CH$_3$|
| 1350                    | 1350    |       |
| 1446                    | 1479    | O-C-O |
| 1479                    | 1479    |       |
| 1518                    | 1510    | O-C-O |
| 1537                    | 1523    |       |

In the uranyl glass Raman spectrum the band with the maximum intensity at the frequency of 1348 cm$^{-1}$ is the most intense. This band corresponds to the excitation of the CH$_3$ group vibration degrees of freedom (see Table 1). The contribution of the UO$_2$ group vibration mode to the observed Raman spectrum is insignificant in comparison with the vibration mode of the CH$_3$ group. At the same time, the PL spectrum of the uranyl glass has phonon repeats with the equidistant phonon shift (850 cm$^{-1}$) corresponding to the fully symmetric mode of the group UO$_2$. 
Figure 4. The PL spectra (a) and RS spectra (b) of the uranyl glass. The semiconductor LED provided optical excitation of luminescence (curve 2) with the wavelength of $\lambda=385$ nm (curve 1). The RS spectra were carried out with the $\lambda=785$ nm CW laser excitation, and the acquisition time was 3 ms.

When the sodium uranyl acetate crystal is excited by the intense laser ($10^9$ W/cm$^2$) with a pulse duration of 80 ps, a repetition rate of 10 Hz and a low pulse energy (1 mJ), intensive combined-frequency satellites with the frequency shift close to the uranyl group (854 cm$^{-1}$) were observed in the secondary emission spectrum. The intensity of the Raman satellites was comparable to the intensity of
the laser radiation line. Thus, in this case the conditions for observing the stimulated Raman scattering (SRS) in the crystals of sodium uranyl acetate are realized. The stimulated Raman scattering was excited at the fully symmetric mode of the uranyl group (\(v_s=854\) cm\(^{-1}\); see Figure 3 a, b). In the (SRS) spectrum the second (2\(v_s\)) and third (3\(v_s\)) Stokes satellites were observed. The first SRS Stokes satellite was strongly attenuated by the filter and was not detected (see Figure 5).

The excitation of sodium uranyl acetate crystal by small energy (0.1 mJ) laser pulses provides the nondestructive manner of SRS observation. The use of the laser sources with the short pulse time and high intensity opens the possibility for the creation of the uranium group UO\(_2\) coherent oscillations of large amplitude during SRS.

![Figure 5: Normalized SRS spectrum of NaUO\(_2\)(CH\(_3\)COO)\(_3\) crystal (curve 2) obtained under excitation by the giant ultrashort pulses of YAG:Nd\(^{3+}\) with the \(\lambda=532\) nm laser (curve 1).](image)

4. Conclusion

Thus, in this paper it is established that in the Raman and photoluminescence spectra the high-quality fully-symmetric mode with the frequency 854 cm\(^{-1}\) is revealed. The developed technique opens the possibility of the uranium compounds express noncontacting detection. The recording of the Raman spectra is provided in a digital form for the small quantity (\(10^{-6}-10^{-8}\) g) substance during 1-10 s. The possibility of the stimulated Raman scattering excitation in the sodium uranyl acetate crystal by means of the YAG:Nd\(^{3+}\) (\(\lambda=532\) nm) laser with short (10-100 ps) and intensive (\(10^9\) W/cm\(^2\)) pulses of laser radiation was estimated.

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