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Spectroscopic properties of U^{3+} ions in a $ZnCl_2$-based glass

P.J. Dereń[a,*], M. Karbowiak[b], J.-C. Krupa[c], J. Drożdżyński[b]

[a] *W. Trzebiatowski Institute of Low Temperatures and Structure Researches, Polish Academy of Sciences, P.O. Box 937, 50950 Wrocław 2, Poland*
[b] *Institute of Chemistry, University of Wrocław, Joliot-Curie 14, 50383 Wrocław, Poland*
[c] *Institute of Nuclear Physics, P.O. Box 1, Bat. 100, 91406 Orsay-Cedex, France*

Abstract

A $ZnCl_2$-based glass sample doped with U^{3+} ions was prepared by mixing $ZnCl_2$, $PbBr_2$, KBr and UCl_3 in an appropriate stoichiometry and by melting the mixture at 450°C under vacuum. Absorption and luminescence spectra of the sample have been measured at 300 and 15 K, respectively. The absorption spectrum is typical for U^{3+} complex compounds in non-aqueous solutions. The emission bands observed at 14 250, 13 100, 8100, 7000 and 4170 cm^{-1} have been assigned to the transitions from the lowest components of the $^4F_{9/2}$, $^4G_{7/2}$, $^4I_{13/2}$, $^4F_{3/2}$ and $^4I_{11/2}$ multiplets to the Stark components of the $^4I_{9/2}$ ground multiplet. Decay curves of the visible emission were strongly non-exponential. The decay time of the longest component of the decay profile was found to be equal to 7 μs and 800 ns at 10 and 300 K, respectively. Good agreement between the observed and calculated oscillator strengths has been obtained in an analysis of the f–f band intensities based on the Judd–Ofelt theory. © 1998 Elsevier Science S.A.

Keywords: Uranium(III); Glass; Spectroscopy; Intensity analysis

1. Introduction

There are only few reports on investigations of glasses doped with trivalent uranium ions. Usually the ions are oxidized during the preparation procedures and enter into a glass as U^{4+} or U^{6+} ions. So far trivalent uranium ions were introduced in glasses [1,2] by reduction of uranium(IV) compounds with γ irradiation. This paper presents spectroscopic investigations of relatively concentrated U^{3+}-doped glasses prepared for the first time by melting together a uranium(III) compound with the appropriate components.

2. Experimental

A glass of the molar composition $0.5ZnCl_2$–$0.4KBr$–$0.1PbBr_2$, doped with UCl_3 to 0.2 and 0.05% has been prepared by melting together the appropriate components. $ZnCl_2$ was purified by vacuum sublimation, UCl_3 was prepared by thermal vacuum decomposition of ammonium tetrachlorouranate(III) tetrahydrate [3]. The appropriate amounts of the anhydrous compounds were sealed under vacuum in a square quartz tube of optical quality. The batch was melted for 30 min at 460°C, then the obtained sample was annealed for 1 h at 60°C and after that was left to cool. Although the difference between the glass transition and crystallization temperature ($T_x - T_g = 70$°C) is not very large, the glass is stable, easily processed and can be doped with uranium ions up to at least 0.5% without crystallization. Unfortunately the resistance of the glass to moisture is poor.

Absorption spectra of a glass sample were recorded on a Cary 5 NIR-Vis-UV spectrophotometer at 300 K. Emission spectra of the sample were measured at various temperatures in the 10–300 K range on a THR 1000 monochromator manufactured by Jobin Yvon and equipped with an R928 photomultiplier. The sample was cooled down in a close cycle helium cryostat. A Qantel YAG:Nd laser, a Carl Zeiss Jena argon laser, and a Lumonics dye laser were used as the excitation sources for measurements of the emission spectra. The decay profiles were recorded using a Lecroy oscilloscope interfaced with a computer and an SR 400 Photon Counter System. A dye laser HD-300 B manufactured by Lumonics excited by an excimer laser, as well as a second harmonic of YAG:Nd laser (532 nm) were used in decay time measurements.

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[*] Corresponding author. Fax: +48 71 441029; e-mail: deren@highscreen.int.pan.wroc.pl

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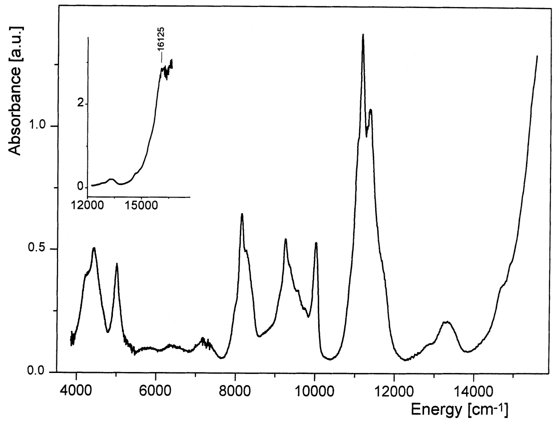

Fig. 1. Room temperature absorption spectrum of the $ZnCl_2$-based glass doped with U^{3+} ions.

3. Results

3.1. Absorption spectra

A crystal field energy level structure analysis for trivalent uranium is much more complex as compared with its neodymium analogue due to a weaker shielding of the 5f electrons by upper orbitals. The crystal field splittings for U^{3+} ions are about twice as large as those for Nd^{3+} ions leading to J mixing. The spin–orbit interaction parameter is about twice as large and the electrostatic interaction parameters are about one-third smaller than those of the neodymium analogue which results in an overlapping of the SL multiplets [4].

Fig. 1 presents the absorption spectra of the $ZnCl_2$-based glass sample doped with U^{3+} ions to 0.2%. In the 4000–15 000-cm^{-1} range one observes a number of $5f^3 \rightarrow 5f^3$ absorption bands which characterize the uranium(III) chloro complex ions [5]. At higher wavenumbers these bands are obscured by strong f–d transitions. One does notice the appearance of the well-separated bands at 4470 cm^{-1} ($^4I_{11/2}$), 7200 cm^{-1} ($^4F_{3/2}$), 8140 cm^{-1} ($^4I_{13/2}$), 9320 cm^{-1} ($^2H_{9/2}$), 9870 cm^{-1} ($^4F_{5/2}$) and 13 065 cm^{-1} ($^4G_{7/2}$). The relatively strong band at about 5002 cm^{-1} is probably due to an impurity present in the sample. The peaks at 5800 and 6440 cm^{-1} have not been attributed, either. The $^4F_{9/2}$ and $^2H_{11/2}$ bands appear on the slope of the f–d absorption bands at 14 670 and 15 470 cm^{-1}, respectively. The centers of the band energy along with the S′L′J′ level assignment and the calculated oscillator strengths of the bands are presented in Table 1. All the peaks, except that at 5002 cm^{-1} are characteristic for U^{3+} ions. They are relatively broad, which can be expected for a glass sample where the investigated ions are situated in different sites.

Table 1
Experimental and calculated oscillator strengths of U^{3+} ions in $ZnCl_2$-based glass

Bands observed in the spectra (cm^{-1})	Level assignment[a] S′L′J′	Center of band energy (cm^{-1})	Oscillator strengths, $P \times 10^6$	
			Exp.	Calc.[b]
4235	$^4I_{11/2}$	4470	1.13	1.13
4420				
4570				
5002	See text			
5800				
6440				
7200	$^4F_{3/2}$	7200	0.16	0.051
7970	$^4I_{13/2}$	8140	1.03	0.94
8140				
8260				
9090	$^2H_{9/2}+{}^4F_{5/2}$	9475	1.74	1.86
9250				
9370				
9560				
9730				
10 002				
11 025	$^4G_{5/2}+{}^4S_{3/2}+{}^4I_{15/2}+{}^4F_{7/2}$	11 300	3.56	3.54
11 150				
11 350				
11 650				
12 835	$^4G_{7/2}$	13 065	0.45	0.23
13 295				
14 670	$^4F_{9/2}$			
14 890				
		r.m.s. $=1.68\times10^{-7}$		

[a] Major component of eigenvector.
[b] Values of the τ_λ parameters obtained in the fitting procedure: $\tau_2=(9.60\pm3.1)\times10^{-10}$, $\tau_4=(3.25\pm3.0)\times10^{-10}$, $\tau_6=(22.95\pm1.5)\times10^{-10}$.

3.2. Intensity considerations

The Judd–Ofelt theory [6,7] of intra f–f transitions has been applied for the intensity consideration. Since the theoretical approach is discussed in numerous articles [7–9] it will not be presented here in detail. The theoretical relationship for the oscillator strength ($P_{\mathrm{E.D.}}$) has been used in a form slightly modified by Carnall for solution spectra [8,9] as shown below:

$$P_{\mathrm{E.D.}} = \frac{\nu}{2J+1} \sum_{\lambda=2,4,6} \tau_\lambda (f^n \psi_J \| U^{(\lambda)} \| f^n \psi'_{J'}) \tag{1}$$

where ν (cm^{-1}) is a particular frequency of the baricenter of a transition (L′J′S′ multiplet), $U^{(\lambda)}$ are matrix elements of the unit tensor operators connecting the initial and final states of the transition (ψ_J and $\psi'_{J'}$) through the complex expressions $\tau_\lambda(\lambda=2,4,6)$. The matrix elements $U^{(\lambda)}$ have been computed by Carnall and are tabulated in Ref. [9]. The τ_λ expressions are treated as parameters to be determined from experiment. For this purpose the $P_{\mathrm{E.D.}}$ values in Eq. (1) have been substituted by the experimental oscillator strengths $P_{\mathrm{exp.}} = 4.318 \times 10^{-9} \int \epsilon(\nu)\,\mathrm{d}\nu$, where $\epsilon(\nu)$ is the molar extinction coefficient at the frequency ν. By using these equations in a least-squares fit, an optimal set of the τ_λ parameters and P_{calc}. has been obtained (Table 1). The six well-separated absorption band areas (Fig. 1, Table 1) were used to evaluate the corresponding oscillator strengths and computation of the τ_λ parameters. In the 8650–10 240 and 10 530–12 280 cm^{-1} absorption range it was not possible to separate the band areas of a particular S′L′J′ multiplet. In these two cases the whole area was measured, one experimental oscillator strength was determined and compared with

$$\sum_i \nu_{\mathrm{av}}[\tau_2 \times U_i^{(2)} + \tau_4 \times U_i^{(4)} + \tau_6 \times U_i^{(6)}],$$

where ν_{av} corresponds to an average center of gravity of all the *i* energy levels (S′L′J′ multiplets) included in the band area. The results are presented in Table 1. So far this has been the second reported [10] case in which the agreement between the observed and calculated oscillator strengths for a uranium(III) absorption spectrum is comparable with those obtained for the lanthanides. Some errors may arise from a degree of arbitrariness in the choice of the centers of gravity of the experimental energy levels (L′S′J′ multiplets) as well as from an imprecise separation of some of the absorption band areas of line groups assigned to these multiplets. In spite of this, no significant change in the obtained values can be expected since their effects seem to be minor.

3.3. Emission spectra

The registered emission bands are shown in Fig. 2. The bands are relatively broad, which is due to emissions from U^{3+} in different sites in the disordered glass structure. The strongest band in the infrared region, with a maximum at 4171 cm^{-1}, has been attributed to the $^4I_{11/2} \rightarrow {}^4I_{9/2}$ transition. The spectrum is similar to that reported for $BaF_2:U^{3+}$ single crystals [11] but exhibits not so well-resolved low-temperature emission bands because of the presence of multiple uranium sites. At 5100 cm^{-1} there appears a weak and broad peak, probably due to transition from another species (compare with the absorption spectrum shown in Fig. 1; peaks at 5002 and 5800 cm^{-1}). The peaks with maxima at 7000 and 8120 cm^{-1} are due to transitions from the $^4F_{3/2}$ and $^4I_{13/2}$ levels to components of the $^4I_{9/2}$ ground state, respectively. The next one at about 10 250 cm^{-1} has been attributed to the $^4F_{9/2} \rightarrow {}^4I_{11/2}$ transition, whereas the two bands with maxima at 13 160 and 14 300 cm^{-1} represent the $^4G_{7/2} \rightarrow {}^4I_{9/2}$ and the $^4F_{9/2} \rightarrow {}^4I_{9/2}$ transitions, respectively. The wavenumbers of the peaks are similar to those observed for U^{3+} in other hosts, but their energies are somewhat higher as compared with those observed in elpasolites where, for example, the $^4G_{7/2} \rightarrow {}^4I_{9/2}$ transition has a maximum at about 12 903 cm^{-1} [12,13], or they are lower than for U^{3+} in $LaCl_3$ where the same transition appears at 13 233 cm^{-1} [4]. This statement holds also for all other transitions, i.e. the energies of the investigated emission peaks are higher then those observed in centrosymmetric crystals but somewhat lower than those reported for the $LaCl_3:U^{3+}$ single crystal.

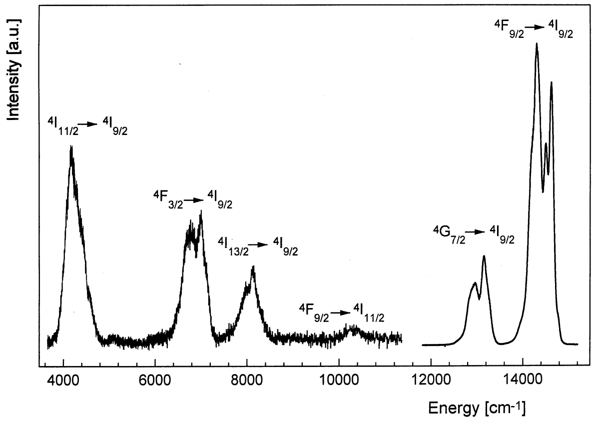

Fig. 2. The 14 K emission spectrum of U^{3+} in the $ZnCl_2$-based glass recorded at $\lambda_{\mathrm{exc}} = 514.5$ nm.

An analysis of transitions from the lowest components of the $^4F_{3/2}$ and $^4G_{7/2}$ multiplets observed in the emission spectra enabled the determination of the Stark splittings of the $^4I_{9/2}$ ground multiplet. The splitting between the lowest ($\mu = 5/2$) and the second component ($\mu = 1/2$) was found to be equal to 140 cm^{-1} and those between $\mu = 5/2$ and the third ($\mu = 3/2$) and fifth ($\mu = 5/2$) components were found to be equal to 360 and 455 cm^{-1}, respectively. The determined values are close to those reported by Carnall and co-workers for $LaCl_3:U^{3+}$ [4].

The presence of multi-sites for the U^{3+} ions in the glass sample is shown in Fig. 3. One can see how the position of the bands in the $^4F_{9/2} \rightarrow {}^4I_{9/2}$ transition energy range is changing along with increasing excitation energy as the

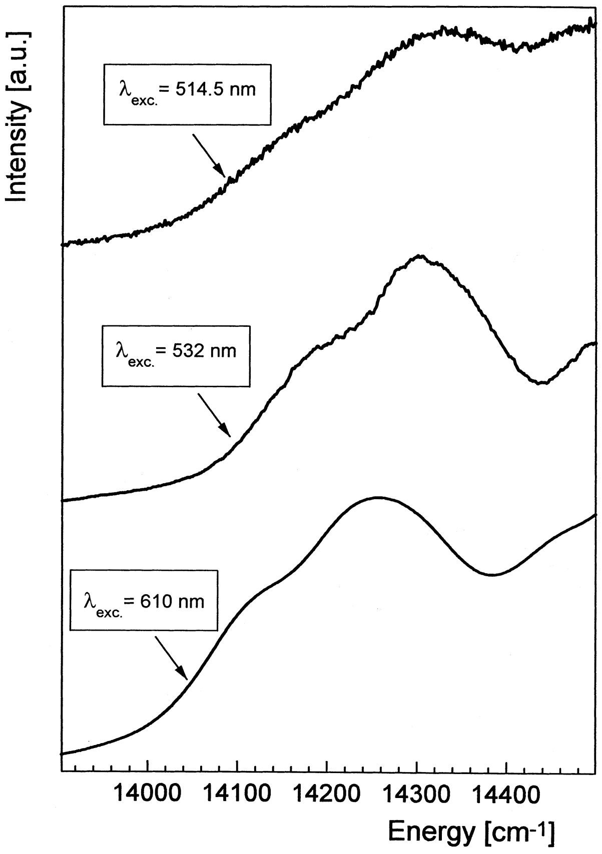

Fig. 3. Site-selective spectroscopy of the ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$ emission of U^{3+} in the $ZnCl_2$-based glass recorded at 14 K.

result of population of different classes of U^{3+} ions. For the 610-nm excitation energy the peak is located at 14 257 cm^{-1}. When the excitation wavelength is tuned to 532 nm and next to 514.5 nm the peak changes its position from 14 300 to 14 331 cm^{-1}, respectively. The emission spectrum of the glass sample might be narrowed using the time-resolved fluorescence line-narrowing technique.

3.4. Decay time measurements

Decay of the visible emission was measured for two excitations: (a) 532 nm where f–d bands were excited and then the excitation energy was nonradiatively transferred to $5f^3$ bands; and (b) 610 nm where a $5f^3$ energy level from the group of the ${}^2K_{13/2} + {}^4D_{3/2} + {}^2H_{11/2}$ states was excited. Fig. 4 shows the emission decay profiles recorded at 15 K at 14 502 cm^{-1}. Curve (a) in Fig. 4 was obtained after 532 nm excitation. As one could expect for a glass sample, the decay curve of the examined emission was strongly non-exponential. Therefore, we have estimated from the decay profiles only the longest and the shortest components.

The observed transfer rate $k_{OBS} = 1/t_{OBS}$ is a sum of the radiative transfer rate k_R, the non-radiative transfer rate k_{NR} which is associated with multiphonon interaction and the energy transfer rate W associated with ion–ion interactions. It may be described by a simple formula:

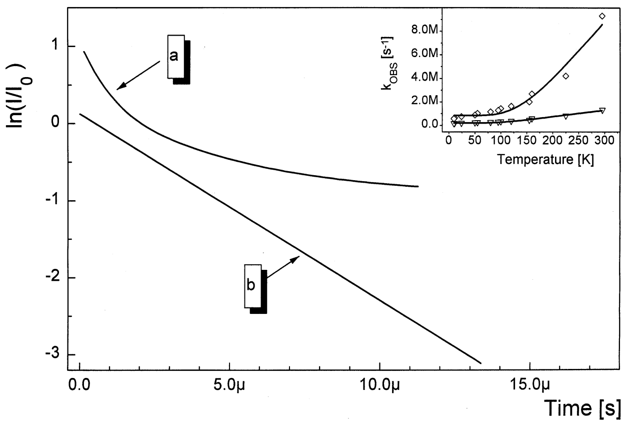

Fig. 4. Decay time profiles of the ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$ emission recorded at 14 K. Curve (a) was obtained under the 532-nm excitation, and curve (b) under the 610-nm excitation. In the inset a dependence of the decay rates after the 532 nm pulse excitation on temperature is shown, the triangles stand for the longest component, the diamonds for the shortest components of the decay profiles. The experimental data were fitted with Eq. (3).

$$k_{OBS} = k_R + k_{NR} + W \qquad (2)$$

The dependence of the observed decay rates on the temperature shown in the inset in the Fig. 4 was fitted by the Arrhenius relation:

$$k_{OBS} = A + s^* \exp(E_a/kT) \qquad (3)$$

where A and s represent the decay rate for $T \rightarrow 0$ and for $T \rightarrow \infty$, respectively, k is the Boltzmann constant and E_a is the activation energy. The best fit was obtained for $A = 1.1 \times 10^5\ s^{-1}$, $s = 4.3 \times 10^6\ s^{-1}$, $E_a = 327\ cm^{-1}$ for the longest components, and for $A = 8.7 \times 10^5\ s^{-1}$, $s = 4.9 \times 10^7\ s^{-1}$ and $E_a = 317\ cm^{-1}$ for the shortest components, respectively. It is concluded that activation energy E_a is similar for all U^{3+} sites and may be associated with the maximum phonon energy of a $ZnCl_2$-based glass, which was found to be 300 cm^{-1} and is markedly lower compared to ZrF_4-based glasses (>500 cm^{-1}) or oxide glasses (>900 cm^{-1}).

When the laser light was tuned to the 610-nm excitation, an interesting phenomenon was observed. It is shown by curve (b) in Fig. 4, where the presented decay profile is one exponential. This result could be obtained when the $5f^3$ bands were selectively excited with a width of the excitation laser light equal to 0.04 cm^{-1}. Hence, it was possible to excite at low temperature the U^{3+} ions occupying only one class of sites. The life time value of 4.3 μs obtained for the ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$ transition is intermediate between these found for the 532-nm excitation. We have to mention that the decay profile of the ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$ emission measured at room temperature is no longer one-exponential, which is due to energy transfer between different U^{3+} ions.

4. Conclusions

For the first time spectroscopic properties of a chloride glass doped with trivalent uranium compounds are presented. The absorption and emission spectra are relatively broad which is due to the presence of many U^{3+} sites in the sample. A good agreement between the experimental and calculated oscillator strengths has been obtained in an analysis of the f–f band intensities, based on the Judd–Ofelt theory. The decay time of the observed emission in the visible region changes from 7 μs at 14 K to 0.8 μs at room temperature.

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