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Abstract—Lifetime of the Nd³⁺ luminescence in POCl₃–TiCl₄–²³⁵UO₂²⁺–Nd³⁺ solutions is almost independent of the concentrations of neodymium and uranyl ions; it attains the maximal value of 220 µs at [TiCl₄] = 0.20–0.35 M and increases with increasing synthesis time, reaching 220 µs at t = 40–60 min. Upon storage, the Nd³⁺ luminescence lifetime decreases by 20–30% in 2 months, and in 2 years it decreases to 60–80 µs in all the samples. Simultaneously with decreasing Nd³⁺ luminescence lifetime, multiple increase in the intensity of the absorption bands of the OH groups is observed in the near-IR range of the absorption spectra of POCl₃–TiCl₄–²³⁵UO₂²⁺–Nd³⁺ solutions.

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This work continues our studies of the properties of liquid phosphors POCl₃–TiCl₄–²³⁵UO₂²⁺–Nd³⁺. Previously [1], the solutions of POCl₃–TiCl₄ activated with ²³⁵UO₂²⁺ and Nd³⁺ ions were prepared and their absorption spectra were studied. Weak bands were recorded in the near-IR range of the absorption spectra, which were not previously found in solutions of phosphorus oxychloride and were identified as first and second overtones of the stretching vibrations of the OH groups. It was found that the intensity of these absorption bands increases with an increase in the synthesis time and in the TiCl₄ concentration in the solution. In this study we measured the Nd³⁺ luminescence lifetime τ in POCl₃–TiCl₄–²³⁵UO₂²⁺–Nd³⁺ solutions and examined the relationship of this parameter with the other characteristics of the solution.

EXPERIMENTAL

The POCl₃–TiCl₄–²³⁵UO₂²⁺–Nd³⁺ solutions were sealed in special quartz or glass cells with the layer thickness l = 0.6–1.2 cm. The Nd³⁺ luminescence lifetimes were measured on a τ-meter equipped with an ISSh-400 gas-discharge pulse high-pressure xenon lamp (τ_pul ≤ 5 µs, f = 10–100 Hz), an FEU-62 single-electron photomultiplier, and an S1-114 oscillograph. The excitation photons were separated using an OS-11 filter. In some cases, excitation was performed with an ILGI-503 pulse nitrogen laser (λ_gen = 337 nm, τ_pul = 20 ns, f = 10–100 Hz). The photons of the Nd³⁺ luminescence were separated with an IKS-1 filter. The accuracy of the τ evaluation was ~10%.

RESULTS AND DISCUSSION

In accordance with published data, the Nd³⁺ luminescence lifetime in POCl₃–TiCl₄–Nd³⁺ solutions is 140 [2] and 210–230 µs [3]. In [4], a series of uranyl-containing samples was prepared by solvation-thermal dissolution of Nd₂O₃ and UO₃ in POCl₃–TiCl₄ (25 : 1 v/v) matrix. Uranium-free POCl₃–TiCl₄–Nd³⁺ solution is characterized by τ = 260 µs. With increasing uranyl concentration from 0.0167 to 0.0667 M and constant content of neodymium, the Nd³⁺ luminescence lifetime decreases from 220 to 180 µs. At a constant uranyl content of 0.0167 M and the neodymium concentration varied from 0.05 to 0.2 M, the luminescence lifetime was approximately constant: τ = 220±10 µs [5].

The data on the Nd³⁺ luminescence lifetimes in POCl₃–TiCl₄–²³⁵UO₂²⁺–Nd³⁺ solutions are shown in Figs. 1–4. In the freshly prepared POCl₃–TiCl₄–Nd³⁺ sample, τ was 200 µs.

At the neodymium concentration [Nd³⁺] varied from 0.06 to 0.30 M, the Nd³⁺ luminescence lifetime remains approximately constant at [UO₂²⁺] = 0.05–0.10 M and [Nd³⁺]/[TiCl₄] = 2.0±0.2 (Fig. 1). With increasing uranyl concentration, τ slightly increases (Fig. 2), but the deviation of the results remains within the range of experimental errors. However, certain
Fig. 1. Nd$^{3+}$ luminescence lifetime as a function of the neodymium concentration in POCl$_3$–TiCl$_4$–$^{235}$UO$_2^{2+}$–Nd$^{3+}$ solutions. [UO$_2^{2+}$] = 0.065±0.025 M; [TiCl$_4$] = 0.3±0.1 M. (1) Freshly prepared solutions and (2) solutions stored for 2 months.

The Nd$^{3+}$ luminescence lifetime strongly depends on the concentration of TiCl$_4$ in solution (Fig. 3) and reaches a maximum (220 μs) at [TiCl$_4$] = 0.20–0.35 M. At [TiCl$_4$] > 0.4 M, τ sharply decreases. As seen from the phase diagram of the POCl$_3$–TiCl$_4$ system [6, 7], the solid phase is formed at room temperature at such concentration of TiCl$_4$ in the liquid.

Let us discuss why the Nd$^{3+}$ luminescence is quenched. It is considered as a proved fact that the hydroxy groups are the only impurity quenchers of the neodymium luminescence in solutions of phosphorus oxychloride [8]. The nonradiative relaxation decreases when the number of the hydrogen bonds in the system decreases. Since the absorption bands of the OH groups observed in [1] overlap with the $^4F_{3/2}$ luminescence level of neodymium ions, its luminescence should be quenched. Hence, the Nd$^{3+}$ luminescence lifetime will decrease with increasing concentration of TiCl$_4$ in POCl$_3$–TiCl$_4$–$^{235}$UO$_2^{2+}$–Nd$^{3+}$ solutions.

However, the result discussed below may look strange. It was found [1] that with increasing time of the synthesis the concentration of the hydroxy groups in POCl$_3$–TiCl$_4$–$^{235}$UO$_2^{2+}$–Nd$^{3+}$ solution increases, whereas the Nd$^{3+}$ luminescence lifetime does not decrease and even increases, reaching a maximum (220 μs) at $t = 40–60$ min (Fig. 4).

We account for this result as follows. It is typical for both neodymium and uranyl ions that their chemical bonds are realized through the same electrons as those excited to provide luminescence. As a result, the electronic excitation of neodymium ions at their incorporation in polymeric molecules becomes collective [5]. The O–P–O bonds act as channels through...