
LASER ABLATION OF THALLIUM COMPOUNDS IN AQUEOUS SUSPENSIONS

S.E. ZELENSKY, O.S. KOLESNIK, B.A. OKHRIMENKO

UDC 535.37, 621.373.8
©2008

Taras Shevchenko Kyiv National University
(2, Build.1, Academician Glushkov Ave., Kyiv 03680, Ukraine; e-mail: zele@univ.kiev.ua)

The optical absorption and the luminescence spectra of aqueous solutions of thallium (I) are investigated. The solutions were produced by means of underwater laser ablation of thallium (III) oxide. The laser ablation is investigated both with and without presence of chlorine ions in the solution. The formation of thallium complexes with chlorine ions is verified by the measurements of UV absorption and luminescence spectra.

1. Introduction

Laser ablation is a well-known method of laser processing which is used, for example, for the production of nanoparticles and thin films [1]. Laser ablation is usually performed under vacuum or in the controllable low-pressure atmosphere. Underwater laser ablation is another method of laser processing which is noticeably less developed and is commonly used for the production of suspensions of nanoparticles [2–8].

In this paper, we investigate the underwater laser ablation of insoluble compounds as a method of preparation of aqueous solutions. As a first step, we have studied the laser ablation of thallium (III) oxide. Thallium is a typical representative of mercury-like elements. Mercury-like ions (MLIs) are those with the configuration of outer electrons similar to the configuration of a mercury atom, $nd^{10}(n+1)s^2$, for example, In^+ , Sn^{2+} , Sb^{3+} ($n = 4$), Tl^+ , Pb^{2+} , Bi^{3+} ($n = 5$). MLIs are widely used in science and technology; hence, a topical question is the development of physical methods for the detection and the monitoring of MLIs, including the methods of optical spectroscopy [9].

In aqueous solutions of some inorganic salts and acids, MLIs form complexes with broadband absorption

and luminescence spectra in the UV and visible regions [10–14]. These spectra are characterized by a complicated structure, which opens up the possibilities for the identification of MLIs by means of the comprehensive investigation of spectra and the kinetics of luminescence. We note that the spectral investigations of MLIs in solutions are often impeded by low solubility of the appropriate compounds, especially for high-valency MLIs (In^{3+} , Sn^{4+} , Tl^{3+} , *etc.*).

2. Experimental Details

The experiments considered in this paper were performed at room temperature with the use of a Q-switched YAG: Nd^{3+} laser (wavelength 1064 nm, pulse duration 15 ns, power density approximately 200 MW cm^{-2} , and repetition rate 12.5 pulses per second). This laser was used for the irradiation of a suspension of Tl_2O_3 particles which was prepared by the continuous stirring of Tl_2O_3 powder in distilled water (2 cm^3) in a 1-cm-thick quartz cell. Within 20–30 min after the laser irradiation, after the suspended particles of Tl_2O_3 settled, the absorption and luminescence spectra of laser-irradiated solutions were recorded under excitation by hydrogen and xenon discharge lamps. For all of the luminescence spectra studied, the excitation wavelength was chosen at a maximum of the appropriate UV absorption band.

For reference, we used thallium aqueous solutions prepared by dissolving TlCl in distilled water and in $(\text{LiCl}+\text{H}_2\text{O})$ electrolyte with the concentrations $C_{\text{TlCl}}=10^{-5}\div 10^{-4} \text{ m}\cdot\text{l}^{-1}$ and $C_{\text{LiCl}}=8 \text{ m}\cdot\text{l}^{-1}$.

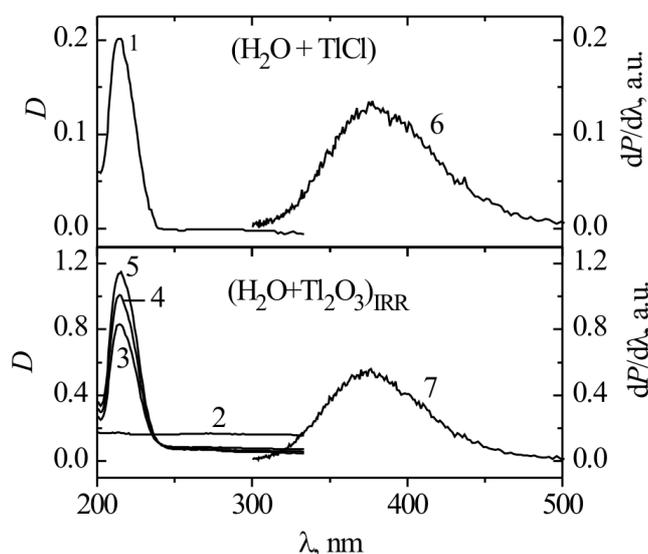


Fig. 1. Absorption (1–5) and luminescence (6, 7) spectra of the aqueous thallium solution ($\text{H}_2\text{O}+\text{TlCl}$) (1, 6) and the aqueous suspension ($\text{H}_2\text{O}+\text{Tl}_2\text{O}_3$) before (2) and after (3–5, 7) the laser irradiation during 1 (3), 2 (4), and 4 min (5, 7). D is the optical density; $dP/d\lambda$ is the spectral density of the luminescence intensity. Subscript “IRR” means laser irradiation. The luminescence excitation wavelength is 224 nm

3. Results and Discussion

As far as thallium (III) oxide is insoluble in water, the spectrum of extinction (absorption and scattering) of the non-irradiated non-settled ($\text{Tl}_2\text{O}_3 + \text{H}_2\text{O}$) suspension (Fig. 1, curve 2) is almost flat and does not show any signs of the UV absorption bands which are characteristic of the aqueous solutions of thallium. After the laser irradiation, this spectrum changes drastically. As is seen from Fig. 1, curves 3–5, a new absorption band located at 214 nm grows with increase in the laser irradiation dose, whereas the “plateau” decreases due to the settling and ablation of suspended Tl_2O_3 particles.

The optical properties of the aqueous solutions with thallium impurities were investigated in detail in [10–14]. For ($\text{H}_2\text{O}+\text{TlCl}$) solutions with low concentration of TlCl , it is accepted that thallium primarily exists in the form of Tl^+ ion enveloped by a shell of H_2O molecules. The solvated Tl^+ ions form the absorption band at 214 nm which is plotted in Fig. 1, curve 1. As is seen from Fig. 1, the absorption spectra of the laser-irradiated ($\text{Tl}_2\text{O}_3 + \text{H}_2\text{O}$)_{IRR} suspensions after settlement (curves 3–5) are similar to the spectrum of the reference ($\text{H}_2\text{O}+\text{TlCl}$) solution (curve 1). This fact suggests that the laser irradiation of insoluble

Tl_2O_3 particles causes thallium to transfer from solid-state Tl_2O_3 into water; hence, the aqueous solution of thallium ions is produced. The experiments show, that the concentration of dissolved thallium increases with the irradiation dose. In our experiments, we achieved the concentrations of dissolved thallium of about 10^{-4} – 10^{-3} $\text{m}\cdot\text{l}^{-1}$ which are usual for aqueous solutions prepared by dissolving the thallium salts. It should be noted that the spectra of irradiated suspensions (Fig. 1, curves 3–5) do not change after a few days of settlement in the cell.

Thallium in aqueous solutions usually exists in two forms: Tl^+ and Tl^{3+} . For example [12], the aqueous solutions of HCl can be easily doped with thallium ions Tl^+ and Tl^{3+} . These solutions are characterized by wide absorption bands in the UV region which look similar for both Tl^+ and Tl^{3+} . This similarity of the Tl^+ and Tl^{3+} spectra can be considered as an indication of the fact that the d -electrons of thallium ions play a significant role in the formation of optical characteristics of thallium-containing compounds. Concerning the luminescence of thallium, it is well known that Tl^+ ions possess luminescence in various wide-bandgap matrices (crystals, glasses, solutions) [15–22]. This luminescence is primarily ascribed to the transitions of the s -electrons of thallium ions, $5d^{10}6s^2 \leftrightarrow 5d^{10}6s6p$. Unlike Tl^+ , thallium ions without s -electrons in the outer shell (Tl^{3+}) do not possess luminescence in electrolyte solutions [12]. This feature gives a possibility to distinguish Tl^+ and Tl^{3+} ions in solutions with the use of the luminescence spectra, rather than the absorption ones.

Our experiments show that the thallium solutions produced by laser ablation demonstrate luminescence typical of Tl^+ ions. As is seen from Fig. 1, curves 6 and 7, the spectrum of luminescence of the ($\text{H}_2\text{O}+\text{TlCl}$) reference solution coincides with the spectrum of the laser-irradiated suspension ($\text{Tl}_2\text{O}_3 + \text{H}_2\text{O}$)_{IRR}. This observed similarity of the luminescence spectra 6 and 7 in Fig. 1 can be considered as an evidence of the formation of dissolved Tl^+ as a result of the laser irradiation of Tl_2O_3 particles suspended in water.

As is known, thallium ions in aqueous solutions are inclined to complexing, for example, with halogen ions. In the presence of surplus chlorine ions in water, the composition of complexes formed by thallium ions depends on the chlorine concentration. With increase in the chlorine concentration, the following layered complexes are formed: $\text{Tl}(\text{H}_2\text{O})_n\text{Cl}$, $\text{Tl}(\text{H}_2\text{O})_n\text{Cl}_2$, $\text{TlCl}(\text{H}_2\text{O})_n\text{Cl}_2$, $\text{TlCl}(\text{H}_2\text{O})_n\text{Cl}_3$, $\text{TlCl}(\text{H}_2\text{O})_n\text{Cl}_4$, $\text{TlCl}_2(\text{H}_2\text{O})_n\text{Cl}_4$ [14], where the number n of water

molecules in the intermediate layer is not known exactly. At high concentrations of chlorine (over 5 mole l^{-1}), the saturated complexes $\text{TlCl}_2(\text{H}_2\text{O})_n\text{Cl}_4$ (with total six chlorine atoms) are dominant in the solution. Complexing in thallium solutions causes significant changes of the spectra and the kinetics of luminescence and absorption. For example, in aqueous solutions of thallium with surplus chlorine, the absorption and luminescence spectra (Fig. 2, curves 1 and 4) are shifted towards the long-wavelength region as compared with the spectra of thallium solutions with low chlorine content (Fig. 1, curves 1 and 6).

In view of the widespread occurrence of chlorinated aqueous electrolyte solutions (for example, seawater), it is of interest to investigate the products of laser ablation of thallium-containing compounds in the mentioned solutions. The results of experiments are given in Fig. 2. Curves 1 and 4 are the spectra of absorption and luminescence of the reference aqueous solution of LiCl doped with TlCl. Spectra 2 and 5 in Fig. 2 were obtained as follows: first, the aqueous suspension ($\text{Tl}_2\text{O}_3 + \text{H}_2\text{O}$) was laser-irradiated, and then LiCl was added in the amount to make a $8 \text{ mole}\cdot\text{l}^{-1}$ solution. On the contrary, spectra 3 and 6 in Fig. 2 were obtained by laser irradiation of Tl_2O_3 particles suspended in the aqueous solution of LiCl ($8 \text{ mole}\cdot\text{l}^{-1}$). We note that it was checked that thallium does not pass from Tl_2O_3 particles into the ($\text{H}_2\text{O} + \text{LiCl}$) solution without laser irradiation.

In Fig. 2, we observe the similarity of the absorption spectra (curves 1–3) and the luminescence spectra (curves 4–6) of the reference and laser-irradiated solutions. This similarity indicates that the saturated thallium complexes $\text{TlCl}_2(\text{H}_2\text{O})_n\text{Cl}_4$ are formed as a result of the laser-induced transfer of thallium ions from Tl_2O_3 particles into the solution. As can be concluded from Fig. 2, the spectral characteristics of laser-produced thallium solutions in ($\text{H}_2\text{O} + \text{LiCl}$) do not depend on whether the laser irradiation of Tl_2O_3 particles was performed in the presence of chlorine ions (Fig. 2, curves 3, 6) or LiCl was added after the completion of the laser irradiation (Fig. 2, curves 2, 5).

4. Concluding Remarks

In this paper, we investigated the optical absorption and luminescence of the products of laser ablation of a Tl_2O_3 powder suspended in water. The main result of these experiments is that thallium solutions with well-known optical properties can be produced by laser irradiation of insoluble thallium compounds. To our opinion, the underwater laser ablation can be of use as a sampling

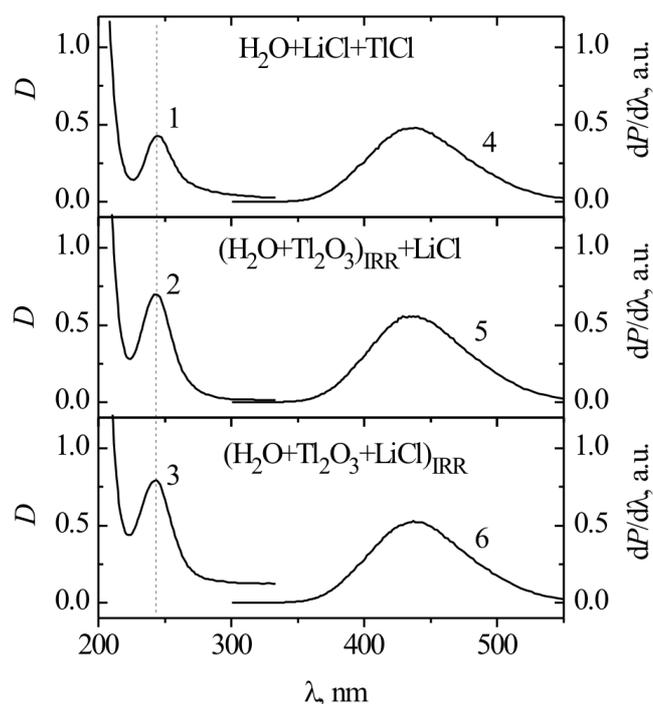


Fig. 2. Absorption (1–3) and luminescence (4–6) spectra of the reference thallium solution ($\text{H}_2\text{O} + \text{LiCl} + \text{TlCl}$) (1, 4) and the laser-irradiated aqueous suspensions ($\text{H}_2\text{O} + \text{Tl}_2\text{O}_3$) (2, 5) and ($\text{H}_2\text{O} + \text{LiCl} + \text{Tl}_2\text{O}_3$) (3, 6). For spectra 2 and 5, LiCl was added after the laser irradiation. For spectra 3 and 6, the irradiation was performed in the presence of LiCl. Subscript “IRR” means laser irradiation. The luminescence excitation wavelength is 240 nm. The laser irradiation duration is 1 min

procedure in some cases of spectral analysis, for example, when a solution of the investigated element is desirable whereas an insoluble compound is given.

1. P.R. Willmott and J.R. Huber, *Rev. Mod. Phys.* **72**, 315 (2000).
2. A. Kruusing, *Opt. and Lasers in Eng.* **41**, 329 (2004).
3. X.P. Zhu, T. Suzuki, T. Nakayama, H. Suematsu, W. Jiang, and K. Niihara, *Chem. Phys. Lett.* **427**, 127 (2006).
4. Y. Ishikawa, K. Kawaguchi, Y. Shimizu, T. Sasaki, and N. Koshizaki, *Chem. Phys. Lett.* **428**, 426 (2006).
5. K.V. Anikin, N.N. Melnik, A.V. Simakin, G.A. Shafeev, V.V. Voronov, and A.G. Vitukhnovsky, *Chem. Phys. Lett.* **366**, 357 (2002).
6. C. Liang, T. Sasaki, Y. Shimizu, and N. Koshizaki, *Chem. Phys. Lett.* **389**, 58 (2004).
7. J.B. Wang, G.W. Yang, C.Y. Zhang, X.L. Zhong, and Z.A. Ren, *Chem. Phys. Lett.* **367**, 10 (2003).
8. N.V. Tarasenko, A.V. Butsen, and E.A. Nevar, *Appl. Surf. Sci.* **247**, 418 (2005).

9. A.K. Das, M. Dutta, M.L. Cervera, and M. Guardia, *Microchem. J.* **86**, 2 (2007).
10. M.U. Bely, I.Ya. Kushnirenko, and B.A. Okhrimenko, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **46**, 373 (1982).
11. M.U. Bely, V.N. Bindiukevich, A.S. Kolesnik, B.A. Okhrimenko, and V.P. Yashchuk, *Sov. J. Appl. Spectr.* **67**, 75 (2000).
12. M.U. Bely and B.A. Okhrimenko, *Ukr. Fiz. Zh.* **6**, 730 (1961).
13. M.U. Bely, N.G. Musienko, and B.A. Okhrimenko, *Ukr. Fiz. Zh.* **19**, 1459 (1974).
14. M.U. Bely, I.V. Zakharchenko, and B.A. Okhrimenko, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **44**, 806 (1980).
15. S. Zazubovich, *Radiat. Measurements* **33**, 699 (2001).
16. P.W.M. Jacobs, *J. Phys. Chem. Solids* **52**, 35 (1991).
17. S. Zazubovich, A. Voloshinovskii, and G. Stryganyuk, *Phys. Status Solidi B* **233**, 238 (2002).
18. L.K. Aminov, A.V. Kosach, S.I. Nikitin, N.I. Silkin, and R.V. Yusupov, *J. Phys.: Cond. Matter* **13**, 6247 (2001).
19. M.U. Bely, B.A. Okhrimenko, and S.M. Yablochkov, *Sov. J. Appl. Spectr.* **34**, 639 (1981).
20. S. Parke and R.S. Webb, *J. Phys. Chem. Solids* **34**, 85 (1973).
21. A.K. Ghosh, *J. Phys. Chem. Solids* **29**, 1387 (1968).
22. M. Bacci, A. Ranfagni, and G. Viliani, *J. Phys. Chem. Solids* **42**, 1021

Received 16.10.07

ЛАЗЕРНА АБЛЯЦІЯ СПОЛУК ТАЛІЮ
У ВОДНИХ СУСПЕНЗІЯХ*С.Є. Зеленський, О.С. Колесник, Б.А. Охріменко*

Резюме

Досліджено спектри оптичного поглинання та люмінесценції водних розчинів талію (I), отриманих шляхом підводної лазерної абляції оксиду талію (III). Досліджено лазерну абляцію у присутності та за відсутності іонів хлору у розчині. Факт формування талієвих комплексів з іонами хлору підтверджено вимірюваннями спектрів ультрафіолетового поглинання та люмінесценції.