RSC Advances

The effect of fullerenes C_{60} and C_{70} on the photo- and triboluminescence of terbium sulphate crystallohydrate in the solid phase

A. A. Tukhbatullin,* G. L. Sharipov and A. R. Bagautdinova

It was found that the addition of C_{60} and C_{70} fullerenes to $Tb_2(SO_4)_3\cdot 8H_2O$ crystals led to a decrease in the photo- and triboluminescence intensities of the Tb^{3+} ion, without affecting the positions of its luminescence maxima. An increase in the intensity of the emission band ascribed to fullerene at 630–850 nm, relative to that without terbium sulphate, was also observed in the photoluminescence spectra. The phosphor luminescence was quenched in a mechanical mixture with the quenchers and luminescence sensitization of the quenchers occurred, indicating that quenching took place in the solid phase by a mechanism similar to that observed in solution; this is due to radiationless energy transfer from the excited Tb^{3+} ion to the C_{60} and C_{70} molecules. The excitation energy is probably transferred through the contacting crystal surfaces of the phosphor and quencher.

Introduction

Currently, fullerene materials are attracting great attention because they can be used in diverse optically active systems such as solar energy converters, laser shutters, and photocells.[1–7] Studying the effects of luminescence activation and quenching in fullerene compositions has become important. Fullerenes are good quenchers of electron-excited states of various organic compounds in solution.[8–11] The quenching of luminescence of trivalent lanthanide ions with fullerenes has also been observed in solution.[12,13] The authors observed highly efficient quenching reactions with fullerenes in solution that have rate constants close to, or even exceeding, that determined by the diffusion limit of 10^{10} L mol^{-1} s^{-1}.[14] Considering this fact, we assumed that quenching of various phosphors with fullerenes could also occur in solid-phase compositions; we observed earlier the quenching of photoluminescence (PL) and triboluminescence (TL, the luminescence of solids during their destruction)[15] in mixtures of terbium sulphate and sodium

nitrite crystals,[16] and the latter is an effective luminescence quencher of lanthanide ions.[14] The aim of this work is to verify this assumption, *i.e.* to study how crystalline C_{60} and C_{70} fullerene additives affect the spectral characteristics and luminescence intensity of excited Tb^{3+} ions for the photo- and triboluminescence of crystalline terbium sulphate. The effect of fullerenes on the luminescence of dinitrogen molecules in the air surrounding the crystals (nitrogen or gas component in TL spectrum)[17,18] will also be examined jointly with the effect of fullerenes on the luminescence of the terbium sulphate crystals (solid-state component in TL spectrum).[15,17–19]

Experimental section

Reagent-grade polycrystalline C_{60} (99.5% Sigma-Aldrich), C_{70} (98% Sigma-Aldrich), $Tb_2(SO_4)_3\cdot 8H_2O$ (99.99% Lanhit) and $NaNO_3$ were used. Samples of the $Tb_2(SO_4)_3\cdot 8H_2O$ crystals (200 mg) were placed in a steel cylindrical cell (25 mm in diameter) with a quartz window at the bottom. For TL excitation, a 4-blade PTFE rod rotating at 1000 rpm was used (the TL setup has been previously described).[16,17,20] The measurement of luminescence was performed while grinding the terbium sulphate crystals with a mixer at the bottom of the steel cylindrical cell at room temperature (295 K) in an air atmosphere, and adding C_{60}, C_{70}, and $NaNO_3$ crystals. The total intensities of the gas and solid-state spectral components of the TL were estimated by using different light filters in a special setup equipped with an "FEU-39" light detector. In the case of photoluminescence, the crystals and their mixtures (after thorough mixing) were placed in a standard 1×1 cm quartz cell and the radiation was detected in the reflection mode. Photoluminescence spectra were recorded with a Fluorolog-3 (Horiba Jobin Yvon) spectrofluorometer (model FL-3-22) equipped with double-grating monochromators, dual lamp housing with a 450 W xenon lamp and a photomultiplier tube detector (Hamamatsu R928P). The PL and excitation spectra were corrected in all cases for source intensity (lamp and grating) and emission spectral response (detector and grating) with the standard instrument correction

High-energy Chemistry and Catalysis Laboratory, Institute of Petrochemistry and Catalysis RAS, 141, pr. Oktyabrya, 450075, Ufa, Russia. E-mail: adiska0501@gmail.com; Fax: +7 347 2842750

provided in the instrument software. The UV-visible absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer using 1 cm quartz cells.

Results and discussion

Fig. 1 shows the dependence of the PL intensity of the terbium sulphate crystals on the amount of C_{60} and C_{70} fullerenes. As can be seen, the addition of fullerenes to the terbium sulphate crystals leads to a strong quenching of the excited Tb^{3+} ion. Thus, the PL intensity of terbium in the presence of fullerene at a 10 : 1 ratio is about 0.5% of the original intensity (Fig. 1), while the positions of the Tb^{3+} luminescence maxima corresponding to the electronic transitions $^5D_4 \rightarrow {}^7F_j$ ($j = 0\ldots6$) are not shifted (Fig. 2).

Such effective quenching of the PL of terbium sulphate crystals in a mechanical mixture with fullerenes is probably due to the quenching mechanism in the solid phase being similar to that observed in solution,[13] *i.e.* it occurs due to nonradiative

energy transfer from the excited Tb^{3+} ion to the fullerene molecule. The increase in the luminescence intensities of the C_{60} and C_{70} fullerenes (Fig. 3), observed in the crystal mixture upon PL excitation in the resonance band of Tb^{3+} at 488 nm and measured in both absorption and emission spectra, also confirms this fact. In a mixture of crystals, the energy is transferred through the contact surfaces of the phosphor and quencher.

Thus, the PL intensity of fullerenes mixed with terbium sulphate is approximately twice as high as the PL intensity of pure C_{60} and C_{70} fullerenes. In addition, a hypsochromic shift of the luminescence maximum is observed in the PL spectrum of C_{60} in the presence of $Tb_2(SO_4)_3 \cdot 8H_2O$ crystals (Fig. 3a). We may assume that the interaction between phosphor and quencher molecules takes place in a similar fashion to the complexation process between them that leads to the redistribution of electron density. As a result, the HOMO–LUMO energy gap of the fullerenes increases, as this gap is responsible for the electronic excitation.[21,22] To ascertain the detailed mechanism of the effect
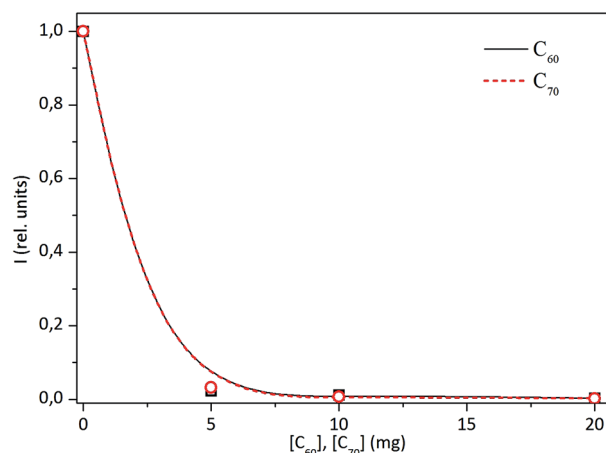

Fig. 1 The dependence of the PL intensity of $Tb_2(SO_4)_3 \cdot 8H_2O$ (200 mg) on the amount of C_{60} and C_{70} added, $\lambda_{exc} = 488$ nm and $\lambda_{lum} = 543$ nm.

Fig. 2 Spectra illustrating the luminescence quenching of $Tb_2(SO_4)_3 \cdot 8H_2O$ with C_{60}. Fluorolog-3, $\lambda_{exc} = 370$ nm and $\Delta\lambda = 0.5$ nm.
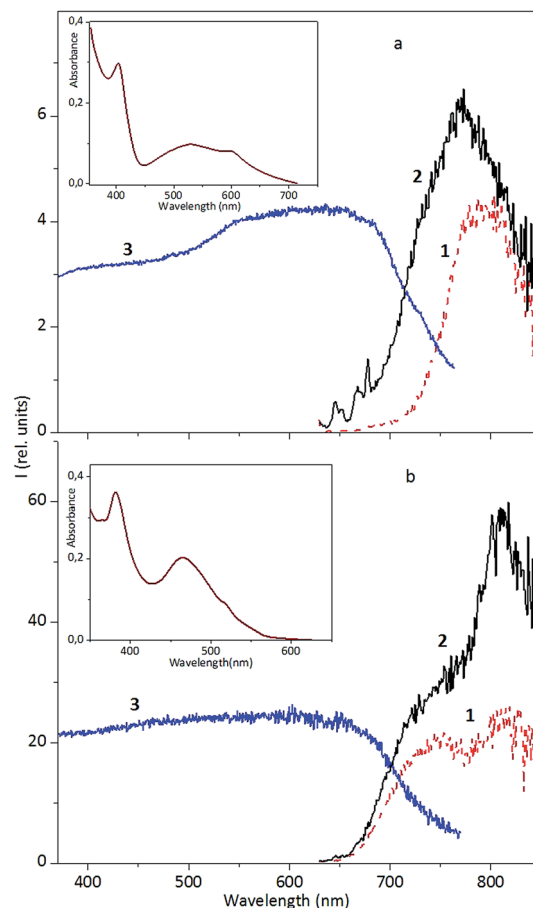

Fig. 3 PL spectra for the emission bands of fullerenes C_{60} (a) and C_{70} (b): (1) pure fullerene without additives and (2) solid-phase mixture of fullerene with $Tb_2(SO_4)_3 \cdot 8H_2O$ at a 1 : 10 ratio; (3) excitation spectra of pure fullerene without additives. For PL spectra, $\lambda_{exc} = 488$ nm; for excitation spectra, $\lambda_{lum} = 750$ nm (C_{60}) and 810 nm (C_{70}). Fluorolog-3, $\Delta\lambda = 2$ nm. The insets show the absorption spectra of fullerenes C_{60} (1×10^{-4} M) and C_{70} (1×10^{-5} M) in toluene at room temperature (295 K).

of terbium sulphate on the PL of C_{60}, further studies are required.

The quenching of excited Tb^{3+} ions is also observed in the TL of a mixture of $Tb_2(SO_4)_3 \cdot 8H_2O$ crystals with fullerenes. However, as compared with PL, the decrease in the luminescence intensity for TL is not so strong. Fig. 4 shows a plot of the intensity of the gas-phase (N_2 is an emitter)[15,17,23,24] and solid-state (Tb^{3+} is an emitter) components of the TL spectrum of $Tb_2(SO_4)_3 \cdot 8H_2O$ against the quantity of C_{60} and C_{70} crystals added.

The TL intensity sharply decreases by half initially, but further addition of fullerene leads to a slight decrease in luminescence intensity. For example, when 20 mg of fullerene is added to 200 mg of terbium sulphate, the TL intensity is five times lower than the initial value, whereas the intensity becomes 350 times lower for PL (Fig. 1).

Considering that electronic phenomena underlie the luminescence caused by the destruction of inorganic lanthanide salts,[15,17] we may assume that in the case of adding fullerenes, their effect is most likely due to the change in the electrophysical properties of the crystal mixture. The small size and high degree of surface curvature of the fullerene molecules, as well as the electrical properties of their crystals (fullerenes are semiconductors with a bandgap of about 1.5–2 eV),[25–27] contribute to the formation of strong local electric fields, resulting in stable electron emission.[28,29]

The strong electric fields arising during the mechanical destruction of crystals on the interface between the terbium sulphate and fullerene, as well as high mobility and charge carrier concentrations, apparently prevent the effective deactivation of the electronically excited states of the Tb^{3+} ion involved in PL.

To confirm the hypothesis that the electrophysical properties of the quencher crystals influence the efficiency of the quenching of TL, we additionally observed that the addition of
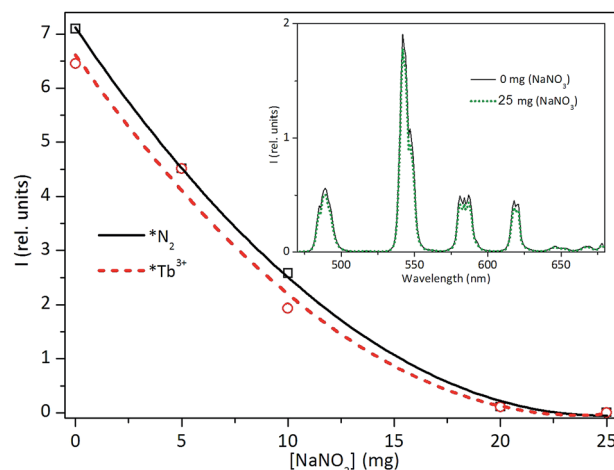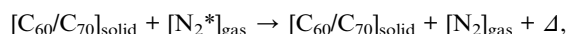

Fig. 5 The dependence of the intensities of the nitrogen ($*N_2$) and solid-state ($*Tb^{3+}$) components of the TL spectrum of $Tb_2(SO_4)_3 \cdot 8H_2O$ (200 mg) on the amount of $NaNO_3$ added. Optical (260–400 nm) and interference ($\lambda = 546$ nm) filters were used for the separation of N_2 and Tb^{3+}, respectively. The inset shows the PL spectra of $Tb_2(SO_4)_3 \cdot 8H_2O$ without (solid line) and with $NaNO_3$ as an additive (short dotted line). Fluorolog-3, $\lambda_{exc} = 370$ nm, $\Delta\lambda = 0.5$ nm.

dielectric sodium nitrate crystals to terbium sulphate in the same ratio (1 : 10) leads to almost complete quenching of TL (Fig. 5), although for PL, quenching of the excited Tb^{3+} ions with sodium nitrate is not observed (Fig. 5, inset). This corresponds to the fact that in aqueous solution, there is no true (except for that caused by the absorption of exciting radiation) quenching of luminescence of the terbium aqua-ion by NO_3^- anions.[30]

In this case, upon TL, adding sodium nitrate, in contrast to fullerenes, leads to a decrease in the conductivity and magnitude of the effective charge accumulated on the terbium sulphate crystal surface.

Conclusions

Thus, addition of C_{60} and C_{70} fullerene crystals to crystalline terbium sulphate leads to strong quenching of the PL of the Tb^{3+} ion, which takes place *via* nonradiative energy transfer to the fullerene molecule. Sensitization of the fullerene luminescence by terbium also confirms this fact. This mechanism of quenching of terbium luminescence is clearly seen for TL. Furthermore, considering that fullerenes quench nitrogen molecules in addition to the luminescence of terbium ions, there is another process of quenching occurring on the crystal surface:

$$[C_{60}/C_{70}]_{solid} + [N_2*]_{gas} \rightarrow [C_{60}/C_{70}]_{solid} + [N_2]_{gas} + \Delta,$$

where Δ is the thermal energy transferred to the crystal.

In the TL process, the quenching effect of fullerenes on the luminescence of terbium ions is weaker than in the PL process, and it is probably due to the electrical nature of the luminescence upon mechanical destruction of the crystals.
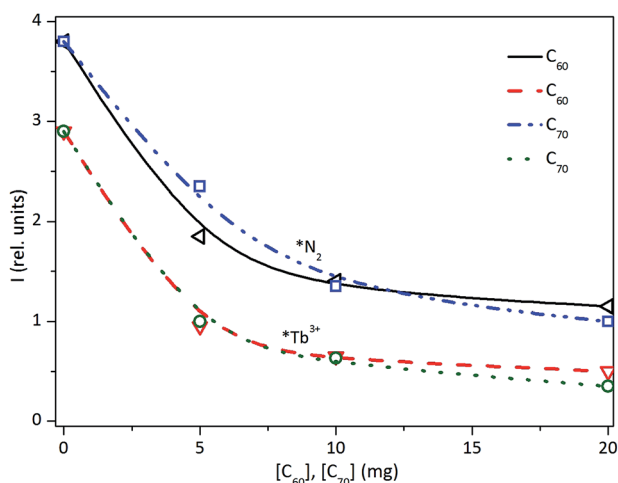

Fig. 4 The dependence of the intensities of the nitrogen ($*N_2$) and solid-state ($*Tb^{3+}$) components of the TL spectrum of $Tb_2(SO_4)_3 \cdot 8H_2O$ (200 mg) on the amount of C_{60} and C_{70} added. Optical (260–400 nm) and interference ($\lambda = 546$ nm) filters were used to extract N_2 and Tb^{3+} luminescence, respectively.

Acknowledgements

Notes and references

1 N. V. Kamanina, L. N. Kaporskii, A. Leyderman and A. Barrientos, *Tech. Phys. Lett.*, 2000, **26**, 279–281.

2 S. Licht, O. Khaselev, P. A. Ramakrishnan, D. Faiman, E. A. Katz, A. Shames and S. Goren, *Sol. Energy Mater. Sol. Cells*, 1998, **51**, 9–19.

3 D. Gust, T. A. Moore and A. L. Moore, *Chem. Commun.*, 2006, 1169–1178.

4 C. Y. Yang and A. J. Heeger, *Synth. Met.*, 1996, **83**, 85–88.

5 R. B. Salikhov, Yu. N. Biglova, Yu. M. Yumaguzin, T. R. Salikhov, M. S. Miftakhov and A. G. Mustafin, *Tech. Phys. Lett.*, 2013, **39**, 854–857.

6 A. Molina-Ontoria, M. Gallego, L. Echegoyen, E. M. Pérez and N. Martín, *RSC Adv.*, 2015, **5**, 31541–31546.

7 H. S. Gill, S. Thota, L. Li, A. Kokil, R. Mosurkal and J. Kumar, *RSC Adv.*, 2015, **5**, 48526–48532.

8 R. N. Nurmukhametov, L. V. Volkova, Yu. I. Kiryukhin, L. V. Romashov and I. E. Kardash, *Dokl. Akad. Nauk*, 1993, **331**, 323–325.

9 J. W. Arbogast, A. P. Darmanyan, C. S. Foote, F. N. Diederich, R. L. Whetten, Y. Rubin, M. M. Alvarez and S. J. Anz, *J. Phys. Chem.*, 1991, **95**, 11–12.

10 R. G. Bulgakov and D. I. Galimov, *Russ. Chem. Bull.*, 2007, **56**, 446–451.

11 R. G. Bulgakov and D. I. Galimov, *Russ. Chem. Bull.*, 2007, **56**, 1085–1087.

12 R. G. Bulgakov, D. I. Galimov, Yu. G. Ponomareva, E. Yu. Nevyadovskii and R. Kh. Gainetdinov, *Russ. Chem. Bull.*, 2006, **55**, 955–960.

13 R. G. Bulgakov, D. I. Galimov and D. Sh. Sabirov, *JETP Lett.*, 2007, **85**, 632–635.

14 J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Plenum Press, New York, 1983.

15 I. Sage and G. Bourhil, *J. Mater. Chem.*, 2001, **11**, 231–245.

16 A. A. Tukhbatullin, G. L. Sharipov, A. M. Abdrakhmanov and M. R. Muftakhutdinov, *Tech. Phys.*, 2013, **58**, 1518–1521.

17 A. A. Tukhbatullin, G. L. Sharipov and A. M. Abdrakhmanov, *Prot. Met. Phys. Chem. Surf.*, 2011, **47**, 13–19.

18 A. A. Tukhbatullin, G. L. Sharipov, A. M. Abdrakhmanov and M. R. Muftakhutdinov, *Opt. Spectrosc.*, 2014, **116**, 691–694.

19 Y. Hasegawa and T. Nakanishi, *RSC Adv.*, 2015, **5**, 338–353.

20 G. L. Sharipov, A. A. Tukhbatullin and A. M. Abdrakhmanov, *J. Lumin.*, 2012, **132**, 175–177.

21 D. A. Sykmanov, Yu. F. Biryulin, L. V. Vinogradova and V. N. Zgonnik, *Semiconductors*, 2001, **35**, 643–647.

22 I. B. Zakharova, V. M. Ziminov, A. V. Nashchekin, Yu. S. Vainshtein and A. N. Aleshin, *Semiconductors*, 2013, **47**, 105–109.

23 G. L. Sharipov, A. A. Tukhbatullin, M. R. Muftakhutdinov and A. M. Abdrakhmanov, *J. Lumin.*, 2014, **148**, 79–81.

24 G. L. Sharipov, A. A. Tukhbatullin and E. S. Mescheryakova, *Opt. Mater.*, 2016, **52**, 44–48.

25 C. P. Jarrett, K. Pichler, R. Newbould and R. H. Friend, *Synth. Met.*, 1996, **77**, 35–38.

26 K. Kaneto, K. Yamanaka, K. Rikitake, T. Akiyama and W. Takashima, *Jpn. J. Appl. Phys.*, 1996, **35**, 1802–1805.

27 T. L. Makarova, *Semiconductors*, 2001, **35**, 243–278.

28 M. E. Lin, R. P. Andres, R. Reifenberger and D. R. Huffman, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 7546–7553.

29 A. V. Tuchin, L. A. Bityutskaya and E. N. Bormontov, *Phys. Solid State*, 2014, **56**, 1685–1688.

30 G. L. Sharipov, R. Kh. Gainetdinov and A. M. Abdrakhmanov, *Russ. Chem. Bull.*, 2003, **52**, 1969–1973.