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Structures, luminescence and vibrational spectroscopy of europium and terbium nitro- and dinitro-substituted benzoates. Nitro groups as quenchers of Ln^{3+} luminescence.

Autorzy

Vera I. Tsaryuk

Valentina A. Kudryashova

Paula Gawryszewska

Roman Szostak

Anna V. Vologzhanina

Konstantin P. Zhuravlev

Z. Klemenkova

Janina Legendziewicz

V. F. Zolin

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Streszczenie

The nitro-substituted benzoates $Ln(NBenz)_3{\cdot}nH_2O$, $Ln(DNBenz)_3{\cdot}nH_2O$, $Ln(NBenz)_3{\cdot}L{\cdot}nH_2O$ and $Ln(DNBenz)_3{\cdot}L{\cdot}nH_2O$ (Ln = Eu, Tb; NBenz = 2- and 4-nitrobenzoate anions, DNBenz = 3,5- and 2,5-dinitrobenzoate anions; L = Phen and Bpy) were investigated by methods of luminescence and vibrational Raman and IR spectroscopy. The crystal structures of $[Eu(4\text{-}NBenz)_3{\cdot}(H_2O)_2]{\cdot}0.5H_2O$ and $[Eu_2(4\text{-}NBenz)_6{\cdot}Bpy_2{\cdot}(H_2O)_2]{\cdot}2H_2O$ (**1**) were solved by X-ray diffraction methods. Known structural data for lanthanide nitrobenzoates are analyzed. The influence of NO_2 groups located in different positions of benzene ring on the structure of Ln^{3+} coordination centre and on processes of the excitation energy transfer to Ln^{3+} ion was studied. The presence of electron-withdrawing nitro groups at aromatic ring of the ligand dramatically decreases Eu^{3+} and Tb^{3+} luminescence efficiencies. This fall amounts to factor $\sim 10^2$ in comparison with europium and terbium benzoates. Low sensitization efficiency of Ln^{3+} luminescence in nitrobenzoates is caused by a dissipation of the excitation energy through the ligand excited state corresponding to transition between the NO_2 oxygen lone pairs orbital and the π* orbital of nitrobenzoate ligand. A low energy of the ligand state in comparison with Tb^{3+} $^5D_4$ state makes for a supplementary reduction of the sensitization of Tb^{3+} luminescence. In ternary compounds, an interligand energy transfer from the Phen or Bpy molecule to nitrobenzoate anion with following quenching due to the nitrobenzoate non-radiative relaxation is observed.

Słowa kluczowe

Eu3+, Tb3+, Nitrobenzoate, atom, 10-Phenanthroline, molecule, 2′-Bipyridine, luminescence, Raman spectra, IR spectra, energy transfer, X-ray crystal structural

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