Role of methylene spacer in the excitation energy transfer in europium 1- and 2-naphthylcarboxylates.

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A series of compounds $Ln(RCOO)_3 \cdot Phen$ (Ln=Eu, Gd, Tb; $RCOO^-$–1- and 2-naphthoate, 1- and 2-naphthylacetate, 1- and 2-naphthoxyacetate anions, Phen–1,10-phenanthroline) was investigated by methods of optical spectroscopy. Compounds of composition $Ln(RCOO)_3 \cdot nH_2O$ with the same carboxylate ligands are also considered. Results of studies of the effects of methylene spacer decoupling the π–π- or p–π-conjugation in the naphthylcarboxylate ligand on the structure of Eu^{3+} coordination centre, on the lifetime of $^5D_0$ (Eu^{3+}) state, and on processes of the excitation energy transfer to Eu^{3+} or Tb^{3+} ions are presented. Introduction of the methylene bridge in the ligand weakens the influence of the steric hindrances in forming of a crystal lattice and results in lowering the distortion of the Eu^{3+} luminescence centre, and in elongation of the observed $^5D_0$ lifetime τ_{obs}. The latter is caused by decrease in contribution of the radiative processes rate $1/\tau_r$. This is confirmed by the correlation between the lifetimes τ_{obs} and the quantities "$\tau_r \cdot$const" inversely proportional to the total integral intensities of $Eu(RCOO)_3 \cdot Phen$ luminescence spectra. The methylene spacer performs a role of regulator of sensitization of the Ln^{3+} luminescence efficiency by means of an influence on mutual location of lowest triplet states of the ligands, the ligand–metal charge transfer (LMCT) states, and the emitting states of Ln^{3+} ions. The lowest triplet state in lanthanide naphthylcarboxylate adducts with Phen is related to carboxylate anion. A presence of the methylene spacer in naphthylcarboxylate ligand increases the triplet state energy. At the same time, the energy of "carboxylic group–Eu^{3+} ion" charge transfer states falls, which can promote the degradation of excitation energy. In naphthylcarboxylates investigated a range of the carboxylate triplet state energies from 19 150 to 20 600 cm^{-1} was demonstrated in dependence on the type of the carboxylate anion. The interligand energy transfer from Phen to carboxylate lowest triplet state was revealed in complexes with Phen ligand. The effect of OH-group inserted in 1- or 3-position of 2-naphthoate ligand on the excitation energy transfer is also analyzed.

Słowa kluczowe

Eu3+, Naphthylcarboxylate, atom, 10-Phenanthroline, luminescence, lifetimes, Triplet states

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