Optical properties of heavy lanthanide maleates in solution and crystal form.

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Monocrystals of $Ln(C_4O_4H_3)_3{\cdot}8H_2O$ (Ln = Eu^{3+}, Ho^{3+}, Er^{3+}) were grown and spectroscopic investigations were performed to understand their photophysical properties. It was found that all the complexes were isostructural with neodymium maleate, $Nd(C_4O_4H_3)_3{\cdot}8H_2O$, whose crystal structure had been determined previously. Electronic absorption and emission spectra at low temperatures for crystals of the lanthanide maleates (with the splitting of the levels) were allowed for the stated lanthanide ions, with a low symmetry environment, in these systems. The intensities of the electronic lines and the Judd–Ofelt parameters were calculated and compared to those obtained for light lanthanides (i.e. Nd(III) and Sm(III)) maleates. The variation of the spectroscopic parameters (e.g. β, δ) and their correlation with the nature of the Ln^{3+}–L bond are discussed. The nephelauxetic ratio β and Sinha's parameter δ suggested an increase in the 'degree of covalency' of the metal–ligand coordination bond from the Eu^{3+} crystal to the Ho^{3+} crystal and to the Er^{3+} crystal of the title compounds. The –CC– double bond in the carboxylate ions determines the distribution of the charge and the character of the Ln–O coordination bonds, which is very important when considering the potential applications of lanthanide carboxylates. In the low-temperature absorption and emission spectra, relatively strong vibronic lines occur, promoted by both ligand (L) and Ln–L localised vibrational modes. In the vibronic coupling, the role of π electrons is not negligible. The emission from the $^5D_1$ level was detected for the europium maleate in spite of the presence of water molecules in the inner coordination sphere of the lanthanide maleate crystals. On the basis of the europium maleate-excited spectra, a ligand-to-metal charge transfer (LMCT) transition was determined at 345 nm.

Słowa kluczowe

lanthanides, maleates, UV-Vis spectroscopy, IR spectroscopy