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ENHANCEMENT LUMINESCENCE OF THE Eu^{3+}-β-DIKETONATE COMPLEXES WITH TERTIARY AMIDES AND DOPED INTO ACRYLIC POLYMER

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In the last years coordination compounds containing trivalent europium ion with high emission quantum yield have been synthesized which have founded several applications in different fields, ranging from photo and electroluminescent devices, polymer optical markers and fluoroimmunoassay reagents. This work reports the synthesis and photoluminescent properties of the β-diketonates complexes with tertiary amides such as dimethylacetamide (DMAC), dimethylformamide (DMFA) and dimethylbenzamide (DMBZ), and the doping of complex into acrylic polymer. The complexes were characterized by elemental analysis, complexometric titration with EDTA, thermogravimetry (TG), differential scanning calorimetry (DSC) and infrared spectroscopy, which suggest the formulas $[Eu(TTA)_3{\cdot}L_2]$ and $[Eu(DBM)_3{\cdot}L]$. The emission spectra of the complexes present the $^5D_0\rightarrow{}^7F_J$ transitions (where J=0-4) dominated by the hypersensitive $^5D_0\rightarrow{}^7F_2$ transition around 612 nm. These transitions are split in the maximum number of (2J+1)-components indicating that the Eu^{3+} ion is in a site of low symmetry. The photoluminescent properties of the complexes were studied based on experimental intensity parameters Ω_2, Ω_4, A_{rad}, A_{nrad} and emission quantum yield (q). The values of the Ω_2 parameters obtained for the DBM-complexes (around 45×10^{-20} cm^2) are larger than those for TTA ones (around 35×10^{-20} cm^2) indicating that the Eu^{3+} ion is in a more polarizable chemical environment in the DBM systems. All the synthesized complexes present values of q higher than 60 %, with particular attention to the Eu-complexes with DMAC and DMBZ ligands that present q values 72 and 82 %, respectively. The $[Eu(TTA)_3{\cdot}(DMBZ)_2]$ complex doped into acrylic polymer (MMA–BA copolymer) gave a transparent and flexible film with high luminescence intensity. The high values of quantum yield suggest that the complexes and the film are strong candidates as Light Conversion Molecular Devices (LCMD's).

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ELECTRIC $4f^N$ ENERGY LEVEL STRUCTURES FOR LANTHANIDE CRYSTAL SYSTEMS: INTRINSIC PARAMETER DETERMINATIONS

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Extensive spectroscopic data for single-crystal lanthanide oxydiacetate systems have been measured for ions across the lanthanide series [1]. Single crystals of $Na_3[Ln(C_4H_4O_5)_3]A2NaClO_4A6H_2O$, grow spontaneously from aqueous solution in two enantiomorphic forms, which differ with respect to the absolute configuration of their constituent $Ln(oda)_3^{3-}$ complexes and the chiral (left-handed or right-handed) arrangement of these complexes about the trigonal symmetry axis of the crystal. Therefore, these systems exhibit chiroptical properties that may be exploited in characterizing spectroscopic state structure and transition mechanisms. Each Ln^{3+} ion is coordinated to three oxydiacetate ligands to form a tris-terdentate chelate structure of trigonal-dihedral (D_3) point-group symmetry. The LnO_9 coordination cluster in each $Ln(oda)_3^{3-}$ complex forms a slightly distorted tricapped trigonal-prism polyhedron, with the top and bottom triangles defined by carboxylate oxygen atoms and the capping positions occupied by ether oxygen atoms.

In this work, information on the coordination geometry is used, along with empirical free-ion and crystal-field parameters determined from the spectroscopic data, to determine radially dependent intrinsic crystal-field parameters for each pairwise interaction between the lanthanide and the coordinated (carboxylate or ether oxygen) ligand atoms. Intrinsic parameter values are calculated for each ion across the lanthanide series, and parameter trends are analysed and discussed.

[1] T. A. Hopkins, D. H. Metcalf. and F. S. Richardson. Inorg. Chem., **1998**, 37, 1401, and references therein.