Vibronic spectra and details of the structure of europium nitrates with derivatives of 1,10-phenanthroline.

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2000

Czasopismo

Journal of Alloys and Compounds

Numer woluminu

300-301

Strony

184-192

DOI

10.1016/S0925-8388(99)00720-3

Kolekcja

Naukowa

Język

Angielski

Streszczenie

Luminescence and excitation of luminescence vibronic spectra as well as IR and Raman spectra of europium nitrates with 1,10-phenanthroline derivatives of formula $Eu(NO_3)_3.Ph_2$ were studied. The effect of size of ligands and their effective charges on crystal structure and, as a consequence, on spectroscopic characteristics was investigated under conditions where one type of ligand (NO_3^- group) is sufficiently rigid. The second ligand, heterocyclic diimine, can change its size and donor-acceptor properties when the substituents are varied. Stark splittings and relative intensities of the Eu^{3+} electronic transitions, the behaviour of vibration frequencies, and vibronic interaction were studied. It was demonstrated that nitrates under investigation have identical composition but form two different structural groups with small and bulky phenanthroline derivatives due to the influence of steric factor. All nitrate anions in the compounds are coordinated and the Eu-O (NO_3^-) bonds are relatively strong. The values of the splitting of stretching vibrations of the NO_3^--anions ($\vartriangle = \nu_4 - \nu_1$) and position of the band of ν(Eu–O) vibration show that the strongest Eu–O bonds are formed in $Eu(NO_3)_3.Nphen_2$, $Eu(NO_3)_3.Tmphen_2$ and $Eu(NO_3)_3.Dphphen_2$ due to high acceptor properties of nitro-phenanthroline and large size of tetramethyl- and diphenyl-phenanthroline molecules. Weak vibronic mixing of electronic and vibronic states was demonstrated in the region of ${}^5D_0$–${}^7F_2$ transition of Eu^{3+}. The vibronic satellites of ${}^5D_0$–${}^7F_0$ -transition due to vibrations of the NO_3^--group borrow about 1–2% of the intensity of the electric-dipole ${}^5D_0$–${}^7F_2$ transition yielding the increase of their relative intensity of 100 times in the Stokes sideband.

Słowa kluczowe

Crystal and ligand fields, Electron-phonon interaction, Luminescence

Typ publikacji

Artykuł

Adres publiczny

https://doi.org/10.1016/S0925-8388(99)00720-3

Strona internetowa wydawcy

http://www.elsevier.com