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The ligand-to-metal energy transfer and the role of Lewis base ligands and silver plasmons in emission of new type of lanthanide phosphors

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ABSTRACT

Two types of new Ln³⁺ chelates, phosphoro- and sulfono-derivatives of beta-diketones and Lewis base ligands were obtained and characterized by the high resolution photoluminescence spectroscopy at 293 and 77 as well as by luminescence decay times. The new type of phosphors shows very strong emission after excitation in the UV range within the ligand bands. The dynamics of the excited state will be discussed. The paths of the energy transfer (ET) are analyzed and mechanism of this process is proposed. The silica gels containing investigated complexes with silver particles were obtained and the role of silver plasmons on spectroscopic properties is displayed.

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1. Introduction

In recent quarter of century, rare earths have become essential for advanced materials and technologies including electronics, economical lighting, optics and lasers, rechargeable hybrid batteries, solar energy conversion, bio-analyses, imaging and others [1–22]. A peculiar aspect of rare-earth applications is that sometimes they are not involved in large quantities. Owing to their special properties, several materials need simple doping of rare earths at low concentration. Moreover, in recent days the challenge is generating highly processed functional materials using minimum amount of these precious elements. Henceforth, the effort is put into elaborating doped polymers, thin films, and nanomaterials [23,24]. Lanthanide(III) β-diketonates and their derivatives are among the most investigated group of the coordination compounds because of their unique luminescence properties, what leads to expansion of applications from wide variety of bioanalytical assays, in diagnostic research, drug discovery, in imaging to electroluminescence diodes (OLEDs) and fluorescence lighting [2,25–35]. Development of efficient organic light emitting diodes (OLEDs) has led to new possibilities for low cost compact

display technology. The use of rare earth ions containing organic molecules is a possible route to obtaining spectroscopic purity for red, green, blue displays with quantum efficiency near 100%. Using appropriate lanthanide complexes for the emission layer, one can achieve electroluminescence covering the spectrum from blue to infrared. Compounds with proper chromophores are the best way to excite metal ion through the forbidden character of f-f transitions.

Sulfonylamidophosphates (SAPh) are the S, N, P-substituted analogs of β-diketones and during the past few years much effort has been devoted to the investigation of the coordination behavior and photophysical properties of this kind of complexes with f-metals [36].

The goal of this paper is focused on obtaining new kind of lanthanide compounds (from the above group) appropriate for OLEDs and solar energy conversion. Thus special behaviors are required for these compounds. In the case of OLEDs materials, the chemical modification of complexes is dictated by three major principles:

1. The complex lower triplet level must match the metal emitting state, being slightly above it.
2. For EL applications, it is considered advantageous to enrich the ligands with electron and hole transporting chemical groups to

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facilitate charge carrier injection and exciton trapping in the complex.

3. The complex must be thin-film formed upon vacuum deposition and thermally stable.

The chelates under study are stable under laser and synchrotron radiations.

Recently we have reported our spectroscopic data and crystal field (C-F) calculations for Nd^{3+} chelate with phosphoroaza derivatives of β -diketones and phosphorylated sulfonylamides. We compared their optical behavior, mainly the radiative transitions probability and the role of character of bonding and M-L distances on intensity changes of f-f transitions and Judd–Ofelt parameters in their spectra [35b]. Now we will pay our attention to the optical properties of two kinds of lanthanide chelates mainly in the aspect of their applicability. The luminescence spectra will be analyzed basing on these X-ray data and role of different physico-chemical parameters on efficiency of emission intensity and energy transfer (fundamental for application) will be considered.

2. Experimental

2.1. Compounds synthesis

The dimethyl(phenylsulfonyl)amidophosphate ligand (HSP) was synthesized in the same manner as described in Refs. [37,38]. The structural formula of the ligand is shown in Fig. 1.

Three series of Eu^{3+} , Gd^{3+} and Tb^{3+} chelates were synthesized with phosphorylated sulfonylamides ($\text{Na}[\text{Ln}(\text{SP})_4]$ where $\text{SP}^- = \text{C}_6\text{H}_5\text{S}(\text{O})_2\text{NP}(\text{O})(\text{OCH}_3)_2^-$) and with Lewis base ligands of the formula $[\text{Ln}(\text{SP})_3\text{Bip}]$ and $[\text{Ln}(\text{SP})_3\text{Phen}]$ (where phen = 1,10-phenanthroline and Bip = 2,2'-bipyridine).

2.1.1. Synthesis of $\text{Na}[\text{Ln}(\text{SP})_4]$

$\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 mmol) was dissolved in acetone (10 mL) and added to 10 mL of acetone solution of NaSP (1.48 g, 4 mmol). After 20 min, the precipitate of NaNO_3 was filtered off, and i-PrOH (10 mL) was added to the filtrate. The resulting clear solution was left at ambient temperature for crystallization in air. Crystals were separated by filtration after 48 h, washed with cool i-PrOH (10 mL), and finally dried in air.

2.1.2. Synthesis of $[\text{Ln}(\text{SP})_3\text{Bpy}]$ and $[\text{Ln}(\text{SP})_3\text{Phen}]$

These complexes were obtained in the similar way by adding isopropanol solution of Lewis base ligand to the mixture $\text{SP}^-:\text{Ln}^{3+}$ (3:1). The complexes are stable in air, thermally stable and soluble in polar organic solvents.

2.1.3. Synthesis of silica-gel materials without silver particles

The silica-gel materials were prepared by slow hydrolysis of TEOS (tetra ethyloorthosilicate) in alcohol–water solutions under presence of small quantity of HCl. Prepared solutions were heated and stirred at a temperature of 50 °C for 1 h up to formation of sol and pH value was adjusted to 5 by the addition of 0.01 M NH_3 . The appropriate amount of the complex in CH_3OH was added to above

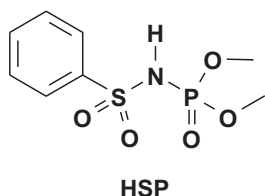


Fig.1. The structural formula of ligand.

sol and stirred. After few weeks almost transparent glass was formed.

2.1.4. Synthesis of silica-gel materials with silver particles

In synthesis of the silica-gel materials codoped with silver particles the same procedure as the above described was applied. The silver particles were incorporated into silica-gel before introduction of solution of the complex to silica-gel. In synthesis of the silica materials codoped by silver particle, the photochemical reduction of silver halide was exploited.

2.2. Measurements

2.2.1. X-ray measurements

The $\text{Na}[\text{Ln}(\text{SP})_4]$ ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$) compounds are isostructural with $\text{Na}[\text{Nd}(\text{SP})_4]$ complex, where lanthanide ion occupies one equivalent position in the structure [36b]. The $[\text{Ln}(\text{SP})_3\text{Phen}]$ ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$) are isostructural with $[\text{Er}(\text{SP})_3\text{Phen}]$ [36c]. X-ray data for $\text{Na}[\text{Nd}(\text{SP})_4]$ and $[\text{Er}(\text{SP})_3\text{Phen}]$ were collected at low temperature using an Oxford Cryosystem device on a Kuma KM4CCD κ -axis diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction and analysis were carried out with the Oxford Diffraction (Poland) programs. The structure was solved by direct methods (program SHELXS97 [39]) and refined by the full-matrix least-squares method on all F2 data using the SHELXL97 [40] programs. Other details of the structure refinement are described in Refs. [36b,c]. The structures of chelates are presented in Figs. 2 and 3.

2.2.2. Spectroscopic measurements

Absorption and reflection measurements were performed using a Cary-Varian 500 spectrophotometer.

Emission spectra were measured with a SpectraPro 750 monochromator equipped with a Hamamatsu R928 photomultiplier and 1200 l/mm grating blazed at 500 nm for Eu^{3+} and Tb^{3+} complexes. A 450 W xenon arc lamp was used as an excitation source, coupled with a 275 mm excitation monochromator using a 1800 l/mm grating blazed at 250 nm. Excitation spectra were corrected for the excitation light intensity, while emission spectra were not corrected for the instrument's response. The luminescence measurements were performed at room and 77 K using a liquid-N₂ cooled Dewar.

The luminescence lifetimes were detected using a Tektronix TDS 3052B oscilloscope and 355 nm and 266 nm lines of Nd:YAG Lambda Physics pulsed laser.

3. Results and discussion

The structures of chelates are presented in Figs. 2 and 3. The compound of formula $\{\text{Na}[\text{Ln}(\text{SP})_4]\}_n$ crystallizes in the monoclinic $\text{P}2_1/\text{c}$ space group [36b]. The molecular structure of the investigated compound is polymeric. Lanthanide ions as well as sodium ions are coordinated by sulfonyl and phosphoryl groups of the ligand, and because of their bridging behavior $[\text{Ln}(\text{SP})_4]^-$ units are linked into the polymer. The structure of $[\text{Ln}(\text{SP})_4]^-$ chelate is composed of LnO_8 coordinate polyhedra. The neodymium chelate crystallizes in monoclinic system with $\text{P}2_1/\text{c}$ space group and the point symmetry of the metal ion is C_{2h} . However, approximation of the coordination polyhedra by method described by Drew [41] shows dodecahedron (Dod) as the closest molecular coordination of Nd^{3+} ion, thus the symmetry should be higher than the X-ray point symmetry for $\text{P}2_1/\text{c}$ space group. Since the $\text{Na}[\text{Eu}(\text{SP})_4]$ chelate is isotopic with $\text{Na}[\text{Nd}(\text{SP})_4]$ chelate, so the same conclusion should be assumed., thus the symmetry of M^{3+} in that chelate is close to D_2 but not higher than D_{2d} [36b].

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