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Luminescence and Magnetic Properties of Europium(III) Nitrate Complex with 1,10-Phenanthroline

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Abstract—Luminescent and magnetic properties of the europium nitrate complex with 1,10-phenanthroline synthesized in the traditional way by precipitation from water–ethanol medium and by the method of mechanical activation were investigated. Correlations between luminescent and magnetic properties of the complex compounds were revealed. The higher value of molar magnetic susceptibility χ_m was shown to be typical for the highly dispersed europium compound obtained by mechanochemistry method due to the presence of the paramagnetic ion Eu^{2+}.

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Earlier [1] we have studied dispersion, surface morphology, and ESR characteristics of the luminescent europium nitrate complex with 1,10-phenanthroline synthesized by the mechanochemistry technique. The data obtained were compared with the characteristics of a complex compound produced in the traditional way by precipitation in a water–ethanol medium. It is known [2] that mechanical activation is an efficient route for the obtaining large quantities of nanopowders of various materials, including alloys, ceramics, composites, etc. The synthesis of nanoparticles by mechanical activation is useful from a practical point of view [3–5].

In this paper we studied the temperature dependence of molar magnetic susceptibility in the temperature range 2–300 K of the complex compounds from europium nitrate and 1,10-phenanthroline synthesized by various methods, and compared magnetic and luminescent characteristics of the complex compounds.

It has been shown in [1] that the europium nitrate complex with 1,10-phenanthroline synthesized by the mechanochemical method is formed as globules of the 100–300 nm size collected into larger aggregates of globular shape or stacked in layers. The ESR method revealed that at the mechanical friction in the material appeared the Eu^{2+} paramagnetic sites [1]. They probably are located on the surface of nanoglobules.

The complex compound $Eu(NO_3)_3 \cdot 2Phen$ synthesized in the traditional way (in water–ethanol medium) consists of a needle microcrystallites 1–20 μm in size. The ESR signal was not found [1].

In this work, for the europium nitrate complex with 1,10-phenanthroline we calculated the Stark structure of $^5D_0$–^7F_j transitions (j = 1, 2) in the luminescence spectra (see the table). The most intense band in the luminescence spectra of compounds corresponds to the extra-sensitive $^5D_0$–$^7F_2$ electric dipole transition

Parameters of luminescencespectra (ν, cm^{-1}) of europium nitrate complex with 1,10-phenanthroline

Transition	Preparation method	
	traditional	mechanical activation
$^5D_0$–$^7F_0$	17212	17210
$^5D_0$–$^7F_1$	16902	16900
	16820	16822
	16714	16715
$\Delta\lambda_{lum}$, cm^{-1}	400	398
$\Delta\lambda_{\chi}$, cm^{-1}	401	377

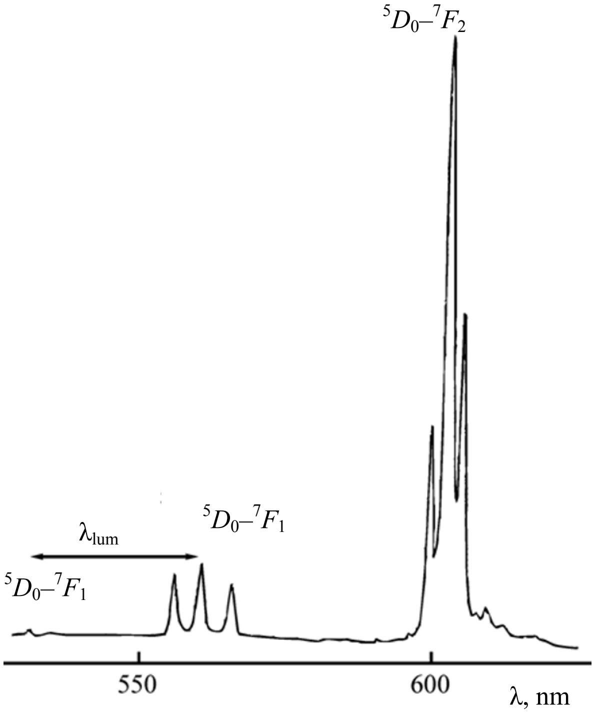

Fig. 1. The luminescence spectrum of the europium nitrate complex with 1,10-phenanthroline.

(612 nm), which is typical for the most of the luminescent europium compounds. In our study we took as the luminescent characteristic the $\Delta\lambda_{\text{lum}}$ value equal to the energy gap between the $^7F_0$ level of the europium ion and the center of gravity of the $^7F_1$ term (Fig. 1) [8]. We also studied the temperature dependence of molar magnetic susceptibility of the synthesized europium compounds in the temperature range 2–300 K (Fig. 2). As can be seen, the magnetic susceptibility varies only slightly in the 300−100 K range.

The Eu^{3+}, in contrast to other lanthanides, has the $^7F_1$ level close to the ground $^7F_0$ (nonmagnetic) level, partially populated at room temperature. The population of this level determines the temperature dependence of χ for the Eu complexes. Using the known Caro–Porcher formula [9] $(\chi_b)_{LT} = 8N\beta^2/\lambda = 2.086/\lambda$, where $(\chi_b)_{LT}$ was the low temperature limit of χ_b value, we obtained the energy gap between the $^7F_0$ and $^7F_1$ levels.

We found that the energy gap λ between the $^7F_0$ and $^7F_1$ levels obtained from the magnetochemical measurements correlate well with fluorescence data (see the table). At the temperatures of 60–50 K the europium nitrate complex with 1,10-phenanthroline exhibits a sharp increase of the molar magnetic susceptibility. This effect may indicate a structural transformation occurring in this temperature range. However, to confirm this hypothesis additional low-temperature spectroscopic and X-ray studies are necessary. It cannot be excluded that this is due to the presence of air in the measuring system [10].

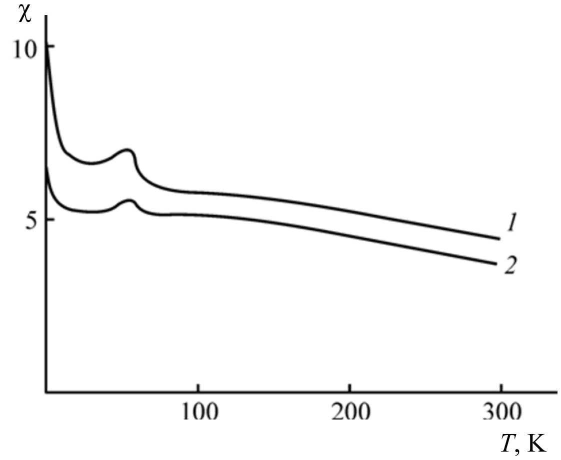

Fig. 2. Temperature dependence of molar magnetic susceptibility of the different-ligand europium compounds: (*1*) $Eu(NO_3)_3{\cdot}2Phen$ synthesized by mechanical activation; (*2*) $Eu(NO_3)_3{\cdot}2Phen$ synthesized in the traditional way (in water–ethanol medium).

As seen from Fig. 2, the molar magnetic susceptibility is higher in the case of the highly-dispersed europium nitrate complex with 1,10-phenanthroline synthesized by mechanochemical method. This europium compound consists of the globules of the size about 100–300 nm. Its ESR spectrum can be assigned to Eu^{2+} (the signal at $g = 2.1$) [1]. As shown by our data, in the case of the compound synthesized by the traditional method the Eu^{2+} ESR signals are absent. It is known that the effective magnetic moment of the Eu(II) ion is twice higher than that of the Eu(III) ion [11].

Thus, the higher value of molar magnetic susceptibility characteristic of highly dispersed complex compound obtained by mechanical activation may be due to the presence of paramagnetic europium(II) ions.

EXPERIMENTAL

We used $Eu(NO_3)_3{\cdot}6H_2O$ and 1,10-phenanthroline of "pure" grade.

The europium nitrate complex with 1,10-phenanthroline was obtained both using the mechanochemistry technique and by the traditional procedure (precipitation from a water–ethanol solution).

The europium nitrate complex with 1,10-phenanthroline was prepared by the method of mechanical activation as follows: europium nitrate and 1,10-phenanthroline in a 1:1 molar ratio, as well as ceramic pebbles were loaded into the drum of a corundum planetary centrifugal mill AGO-2 [6]. The ratio of payload to the ceramic pebbles weight was 1:3, the drum volume 150 cm^3. The starting compounds were subjected to vibration (1000 rpm) for 1–10 min. After one minute sampling of the reaction mixture was performed for the physicochemical study. The resulting europium nitrate complex with 1,10-phenanthroline was washed with water–ethanol mixture (1:1) to remove soluble reaction products and unreacted starting components. The precipitate was filtered off and dried at 20°C.

By the traditional way the europium nitrate complex with 1,10-phenanthroline was synthesized as described in [7].

Molar magnetization of the complexes was measured on a magnetometer SQUID MPMS 7 at temperatures 2–300 K in a magnetic field of 1000 Oe. The luminescence spectra of europium compounds were measured at 77 K on a SDL-1 spectrometer with a mercury lamp DRT-250 (filter UFS-6). The ESR spectra were recorded on an ESR spectrometer RE 1306.

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