



Photoacoustic spectrum of Er(III) in Er₂O₃



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Abstract

The photoacoustic (PA) spectrum of the f-f transitions in Er₂O₃ have been recorded at room temperature. The PA spectrum, consisting of many absorption lines in a visible region of the electromagnetic radiation, has been compared with PA spectra of Er-hydrazone and Er-hydrazine complexes. For erbium organometallic complexes and Er₂O₃ the most intense PA line is observed at 525 nm (⁵I_{15/2} - ²H_{11/2}). The PA spectroscopy has shown that the relaxation processes connected with erbium(III) f-f-transitions strongly depend on the kind of matrix.

Introduction

Erbium(III) ion (4f¹¹) plays a very important role in many electronic systems. Organometallic rare earth(III) complexes are used in biological/pharmaceutical applications due to their antimicrobial, antitumor, antituberculous and anticancer activities [1-7]. Previously, we have reported the photoacoustic (PA) spectral characterization of rare earth-hydrazone/hydrazine complexes with different coordination number for which in a visible region of radiation the intense f-f transition absorption lines were registered [8-11]. The organometallic 4f rare earths(III) and 3d transition ions(II) complexes studied by the PA method provide additional experimental results connected with the dynamical processes (the intermolecular energy transfer or the heating processes) correlated with the photon-electron-phonon interactions [8-13]. The intensities of the f-f PA absorption lines strongly depend on the kind of organic matrixes [11]. The PA absorption spectra present a collection of very narrow lines (localized wavefunctions) with positions practically unaffected by the replacement of the surrounding ligands in opposition to the d-d transitions producing very broad lines. The analysis of the values of the Judd-Ofelt intensity parameters for erbium(III) ions in a fluorine containing (Pb, La)-tellurite glass has shown essential differences connected with elemental and structural properties in different glasses samples [14]. The erbium oxide (Er₂O₃) as dopant in organic matrix is a very promising potential candidate for an optical image storage and holography and the intensities of PA absorption lines change drastically [15,16].

The aim of this paper is to report on the PA absorption lines of the f-f transitions in Er₂O₃ compound and to compare the PA spectrum to PA response of other erbium(III) complexes, particularly erbium(III) hydrazone/hydrazine complexes.

Experimental

The erbium oxide (sesquioxide Er₂O₃) is crystallized into C-type cubic structure [17].

PA spectrum of polycrystalline powder samples has been obtained using a modification of the PA spectroscopy method, initially proposed by G.J.Papadopoulos and G.L.R.Mair [18]. A Xenon arc lamp with 1 kW power and a 1/4m ORIEL monochromator were used as a light source, with bandpass width of 5 nm (at 500 nm). The light, intensity modulated using a mechanical chopper at frequency of 10 Hz was directed into a photoacoustic cell equipped with a TREVI EM27 microphone. A dual SR830 lock-in amplifier measured amplitude and phase of the PAS signal detected by the microphone. Data acquisition ensured that each value was an average of 20 runs at the same wavelength of the incident light. A carbon black was used as a standard to re-calibrate the final spectrum. The PAS of the compound was recorded at room temperature, in 300 – 700 nm range.

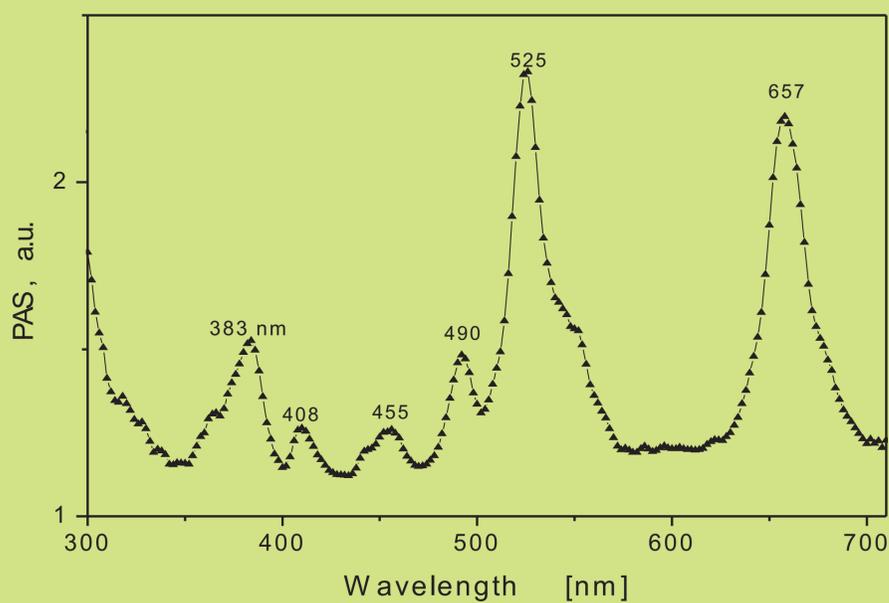


Figure 1. Photoacoustic spectrum of Er(III) in Er₂O₃.

Table 1. The positions (λ_i) and relative intensities (I_i/I_5) of absorption lines of erbium(III) ions in different matrixes.

sample	Er ₂ O ₃ [this work]	Er ₂ O ₃ [14]	Er-hydrazine [8]	Er-hydrazone [13]	Er _{op} -tellurite glass [16]
λ_1 [nm]	383	381			379
λ_2 [nm]	408	407	~420		408
λ_3 [nm]	455	457	~450		452
λ_4 [nm]	490	489	484	485	490
λ_5 [nm]	525	524	523	522	522
λ_6 [nm]	545	546	~547	~546	544
λ_7 [nm]	657	656	657	657	653
I_1/I_5	0.31	0.42			1.16
I_2/I_5	0.11	0.27	<0.03		0.03
I_3/I_5	0.11	0.21	<0.03		0.03
I_4/I_5	0.26	0.46	0.23	0.25	0.16
I_6/I_5	0.34	0.27	<0.05	<0.04	0.05
I_7/I_5	0.86	0.63	0.38	0.35	0.29

Conclusions

Comparison of the peak positions attributed to the f-f transitions of erbium(III) ion allows to draw conclusion that, within experimental errors (which are around 200 cm⁻¹), the positions are unchanged by the change of matrix. Another situation is encountered in case of relative intensities, which differ substantially for complexes of erbium(III) ions. The intensities of the PAS peaks rare earth ions are depended strongly from spurious phases as well from the kind of the matrix where It is very important for the dynamical processes connected with intermolecular transfer energy.

Results and discussion

Figure 1 presents the PA spectra of erbium(III) ions in Er₂O₃ compound in the 300-700 nm range with the following electron f-f transitions: ⁵I_{15/2} - ⁵G_{11/2} (1), ⁵I_{15/2} - ²H_{9/2} (2), ⁵I_{15/2} - ⁴F_{3/2} (3), ⁵I_{15/2} - ⁴F_{7/2} (4), ⁵I_{15/2} - ²H_{11/2} (5), ⁵I_{15/2} - ⁴S_{3/2} (6) and ⁵I_{15/2} - ⁴F_{9/2} (7). The position and the relative intensities of Er₂O₃, compared to other Er(III) complexes are given in Table 1. The position of the electron transitions are almost the same, independently on kind of matrix and the used technique of measurements (PA or UVVIS) in contrast to line intensities that differ significantly (see Table 1). The most intense PA line is due to the transition ⁵I_{15/2} - ²H_{11/2} while in optical measurements the transition ⁵I_{15/2} - ⁵G_{11/2} is most intense [14]. Substitution of erbium(III) ions in other matrixes causes essential changing of relative intensities of PA lines in comparison to Er₂O₃ (Table 1). The essential differences of relative intensities PA lines are shown on the same Fe₂O₃ (Table 1). It is suggested that the spurious phases could be influenced essential on the relaxation processes of intermolecular transfer energy.

The PA spectrum is the result of heat generated through the nonradiative transitions in a solid sample after absorption of periodically varying incident light. The relaxation processes could be considered as radiative and nonradiative after excitation of electrons by the electromagnetic radiation. The observed PA lines are due to the nonradiative processes which could involve directly the localized levels of ions. The intensity of the PA line might be given by the expression, $I = k A_{abs}$, where k is a coefficient determined by the thermal properties of the material and the spectrometer, A_{abs} is the absorbance of sample, and γ is the probability of non-radiative transitions after excitation by electromagnetic radiation. Different matrixes generate different coefficients k and A_{abs} , but the relative intensities of PA signals should have similar values. If it is supposed that the main contribution arises from γ and is connected with the non-radiative transitions. A specific kind of matrix should reveal itself in the electron-vibration interaction that is much stronger than in erbium oxides [13]. This could have a large influence on strong PA lines. Numerous, closely packed energy levels of erbium(III) ions are often intermixed and with high probability the excitation can relax through the nonradiative processes. An electron is promoted from the ground excited levels inside 3f¹¹ shell, the resulting 4f - 4f intra-configuration transitions usually give weak and sharp peaks that could be influenced by a specific type of matrix. The dynamic crystal field and the electron-phonon coupling could be changed by different lattices and influence effectively the relaxation processes. The organic hydrazone/hydrazine complexes with erbium have produced essential differences in their intensities [8,16] but the relative intensities are almost the same (Table 1). In this case the coefficients k and A_{abs} play a very important role.

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