

RELATIVE INTENSITIES OF f-f TRANSITIONS OF ERBIUM(III) ION STUDIED BY PHOTOACOUSTIC SPECTROSCOPY

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Abstract. A photoacoustic (PA) spectrum of the f-f transitions in Er₂O₃ was recorded at room temperature. The PA spectrum, consisting of many absorption lines in the visible region of the electromagnetic radiation, was compared with the PA spectra of Er-hydrazone and Er-hydrazine complexes. The most intense PA line for erbium organometallic complexes and Er₂O₃ was observed at 525 nm (⁶I_{15/2} → ²H_{11/2}). The PA spectroscopy showed that the relaxation processes connected with the erbium(III) f-f transitions could strongly depend on the type of the used matrix and on the preparation conditions. The thermal annealing process could influence the creation of different defects which could influence the PA spectra of rare earth(II) ions, especially their relative intensities. The proposed method can be used for characterization of materials by studying the relative intensities of spectral lines produced by the introduction of rare earth(III) ions (with localized wavefunctions) with the PA spectra in the visible region of radiation.

1. 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, antituberculostatic and anticancer action [1-7]. The compound Er₂O₃ is one of the most extensively investigated materials since its optical properties show promise for extensive applications, e.g. [8-12]. We have previously reported on the photoacoustic (PA) spectral characterization of rare earth-hydrazone/hydrazine complexes with different coordination numbers for which absorption lines of an intense f-f transition were registered in the vis-

ible region of radiation [13-16]. Organometallic complexes of 4f rare earths(III) and 3d transition ions(II) studied by the PA method provide additional experimental results connected with the dynamical processes (intermolecular energy transfer or heating processes) correlated with the photon-electron-phonon interactions. The intensities of the f-f PA absorption lines strongly depend on the type of the organic matrices used [16]. The PA absorption spectra present a collection of very narrow lines (localized wavefunctions) with their positions practically unaffected by the replacement of the surrounding ligands in contrast to the d-d transitions which produce very broad lines. An analysis of the Judd-Ofelt

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intensity parameters for erbium(III) ions in a fluorine-containing (Pb, La)-tellurite glass has shown essential differences connected with the elemental and structural properties in different glass samples [17]. The erbium oxide (Er_2O_3) as a dopant in an organic matrix is a very promising potential candidate for optical image storage and holography because the intensities of the PA absorption lines change drastically with the type of the matrix [18,19].

The aim of this paper is to report on the PA absorption lines of the f-f transitions in an Er_2O_3 compound and to compare its PA spectrum to the PA response of other erbium(III) complexes, in particular, erbium(III) hydrazone/hydrazine complexes. It is expected that the main change could be observed in the relative line intensities since the localized wavefunctions are not sensitive to the local surroundings.

2. EXPERIMENTAL

Erbium oxide (sesquioxide Er_2O_3 from Aldrich with the purity of 99.999%) crystallizes into a C-type cubic structure (space group $\text{Ia}\bar{3}$, $a = 10.53 \text{ \AA}$) [20]. Before the experiments, Er_2O_3 was heated at $850 \text{ }^\circ\text{C}$ for a 30-h period to eliminate any trace amounts of water and CO_2 .

The PA spectrum of polycrystalline powder samples was obtained using a modification of the PA spectroscopy method, initially proposed by G.J. Papadopoulos and G.L.R. Mair [21]. A 1 kW Xenon arc lamp with was used as the light source and a 1/4m ORIEL monochromator had a bandpass width of 5 nm (at 500 nm). The light intensity, modulated using a mechanical chopper at a frequency of 10 Hz, was directed into a photoacoustic cell equipped with a TREVI EM27 microphone. The amplitude and phase of the PA signal detected by a microphone were measured by a dual SR830 lock-in amplifier. The data acquisition method ensured that each data point was the average of 20 runs for the same wavelength of incident light. Carbon black was used as a standard to re-calibrate the final spectrum. The PA spectra of the compound were recorded at room temperature in the 300 – 700 nm range.

3. RESULTS AND DISCUSSION

Fig. 1 presents the PA spectra of erbium(III) ions in an Er_2O_3 compound in the 300-700 nm range. The following electron f-f transitions could be recognized:

$^4\text{I}_{15/2} \rightarrow ^5\text{G}_{11/2}$ (1), $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{9/2}$ (2), $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{3/2}$ (3), $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$ (4), $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ (5), $^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$ (6) and $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ (7). The position and the relative intensi-

ties of Er_2O_3 compared to other Er(III) complexes are given in Table 1. The positions of electron transitions are almost identical, independent of the kind of the matrix and the measurement technique used (either PA or UV/VIS) in contrast to line intensities that differ significantly (Table 1). The most intense PA line is due to the transition $^5\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ while the transition $^4\text{I}_{15/2} \rightarrow ^5\text{G}_{11/2}$ is the most intense in optical measurements [17]. The substitution of erbium(III) ions in other matrices causes a substantial change in the relative intensities of the PA lines in comparison to the Er_2O_3 compound (Table 1). The essential differences of the relative intensities of the PA lines are shown on the same Er_2O_3 but originating from a different manufacturer (Table 1). It is suggested that the spurious phases or defects could essentially influence the relaxation processes of intermolecular transfer energy, especially as far as relative intensities are concerned.

The PA spectrum is a result of heat generated through nonradiative transitions in a solid sample after absorption of incident light of periodically varying intensity. The relaxation processes could be considered as radiative or nonradiative after excitation of electrons by the electromagnetic radiation. The observed PA lines are due to the nonradiative processes which could directly involve localized levels of ions. The PA line intensity can be given as $I = kA_{\text{abs}}\gamma$, where k is a coefficient determined by the thermal properties of the material and the spectrometer, A_{abs} is the sample absorbance and γ is the probability of non-radiative electron transitions after excitation by electromagnetic radiation. Different matrices are characterized by different coefficients k and A_{abs} , but the relative intensities of PA signals should have similar values. If we suppose that the main contribution arises from γ and is connected to the non-radiative transitions, the relative intensities between different electron transitions could change. A specific kind of a matrix where erbium(III) ions are introduced should display an electron-vibration interaction much stronger than in erbium oxides [16]. This can have a large influence on strong PA lines. Numerous, closely packed energy levels of erbium(III) ions are often intermixed and the excitation can, with high probability, relax through the nonradiative processes. An electron is promoted from the ground excited levels inside a $3f^{11}$ shell, the resulting $4f \rightarrow 4f$ intra-configuration transitions usually give weak and sharp peaks that could be influenced by a specific matrix type. The dynamic crystal field and the electron-phonon coupling could be changed by application of different lattices and effectively influence the relaxation processes. The

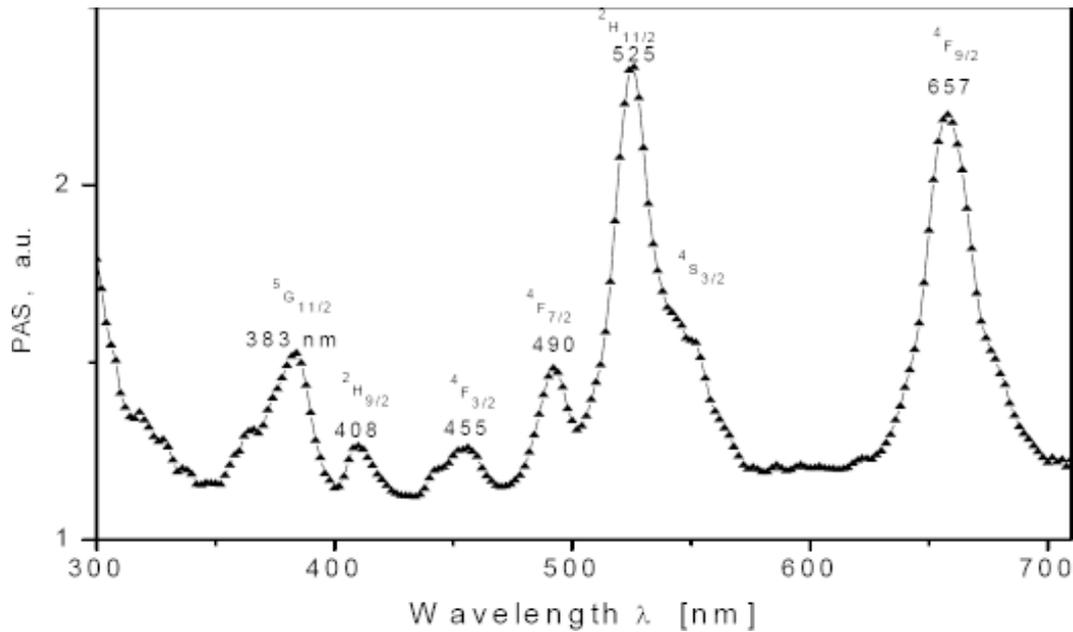


Fig. 1. Photoacoustic spectrum of Er(III) in Er_2O_3 .

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

	Er_2O_3 [this work]	Er_2O_3 [17]	Er-hydrazine [8]	Er-hydrazone [16]	Er_{op} -tellurite glass [19]
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

organic hydrazone/hydrazine complexes with erbium have shown essential differences in their intensities [8,19] but the relative intensities are almost identical (Table 1). In this case the coefficients k and A_{abs} play a very important role in determining the intensity of PA transitions.

The localized wavefunctions of the rare earth(III) ions cause a slight change in the position of the PA

lines while a strong dependence on the complex type is observed in the transitions ions (with extended wavefunctions) [22,23]. PA spectroscopy could prove itself a very useful method for characterization of samples containing rare earth(III) ion complexes. The same complex subjected to a different thermal annealing process could produce different relative intensities in its PA spectra. This could

be connected with the presence of defects or some localized imperfections lowering the symmetry near rare earth(III) ions. This is of great concern in optoelectronic applications, in particular those involving laser transitions.

Optical absorption spectra of erbium(III) in different glasses have shown that the relative intensities remain the same [24-26]. Furthermore, the absorption line of the electron transition $^4I_{15/2} \rightarrow ^4F_{9/2}$ is lower in contrast to the more intense transition $^4I_{15/2} \rightarrow ^5G_{11/2}$. The thermal processes in PA spectroscopy could provide important information on the dynamic processes in materials. The discrepancies between our results and those reported by others, mainly observed in relative intensities, probably result from a different state of defects in the studied materials [16,17]. This method could be very useful for characterization of very important materials used for application in optoelectronics containing erbium ions.

4. CONCLUSIONS

A comparison of the peak positions attributed to the f-f transitions of erbium(III) ion makes it possible to draw a conclusion that the positions, within experimental errors (of approx. 5 nm), are essentially unchanged by an alteration of the used matrix. Another situation is encountered in the case of relative intensities which differ substantially for various complexes of erbium(III) ions. The intensities of the PA peaks for rare earth ions depend strongly on spurious phases as well as on the matrix type. This is related to the dynamical processes connected with intermolecular transfer energy. The differences among relative erbium(III) ion intensities in the optical spectra obtained by different methods (UV-VIS and PA spectroscopy) could be connected with the fact that the detection of acoustic waves depends on the thermal processes inside the sample. This, in turn, depends on the matrix and thus essentially influences the kind of the involved electron transitions.

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