

Optical absorption and spectroscopic characterization of Er³⁺ ions in lead molybdate crystals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 6585

(<http://iopscience.iop.org/0953-8984/13/30/314>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 14:01

Please note that [terms and conditions apply](#).

Optical absorption and spectroscopic characterization of Er³⁺ ions in lead molybdate crystals

N R Aghamalyan¹, R B Kostanyan and T V Sanamyan

Institute for Physical Research NAS of Armenia, Ashtarak-2, 378410, Armenia

E-mail: natagam@ipr.sci.am (N R Aghamalyan)

Received 19 April 2001

Published 13 July 2001

Online at stacks.iop.org/JPhysCM/13/6585

Abstract

The main spectroscopic characteristics of PbMoO₄:Er³⁺ crystal, including the probabilities of the intermultiplet transitions and the radiative lifetimes of Er ions in the crystal based on the analysis of (π - and σ -) polarized absorption spectra using the Judd–Ofelt theory, are determined. The effective Judd–Ofelt parameters obtained for Er³⁺ ions in PbMoO₄ crystal are $\Omega_2 = 4.10 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 0.51 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.20 \times 10^{-20} \text{ cm}^2$. A comparison of the calculated radiative lifetimes with experimentally measured luminescence decay times is carried out. The experimental diagrams of the Stark sublevels of some multiplets of Er³⁺ ions in PbMoO₄ crystal are obtained and the optical transitions between them are identified.

1. Introduction

The interest in activated materials with multifunctional properties has recently increased because of the utilization of lasers based on these materials in integrated optics and the miniaturization of optoelectronic devices. The possibility of combining laser emission and electro-optical and acousto-optical properties will allow the creation of a compact solid-state laser, which combines the different functions in the laser crystal itself.

Er³⁺ is a well-known laser ion with optical transitions in the infrared as well as in the visible wavelength range. The combination of the excellent acousto-optical properties of PbMoO₄ along with the possibility of rare-earth doping has stimulated interest in this material as regards photonic applications.

Lead molybdate crystals have the scheelite-type structure with the space group $I4_1/a-C_{4h}^6$. The symmetry point group of Er³⁺ impurity in PbMoO₄ crystal is S₄. In this work, we give the results obtained by applying the Judd–Ofelt treatment to anisotropic materials, in order to provide an understanding of the basic optical properties of Er³⁺ ions in PbMoO₄ crystals.

¹ Author to whom any correspondence should be addressed.

It is found that the results are strongly polarization dependent. Additionally, experimental lifetimes are also analysed and compared with Judd–Ofelt predictions.

2. Experimental procedure

Er-doped PbMoO₄ crystals were grown by the Czochralski method. The dopant, as erbium oxide, was added to the melt. Details of the growth procedure and initial spectroscopic data have been given previously in [1]. The erbium concentrations in the crystals were measured at the Central Service d'Analyse (Vernaison, France). The erbium concentrations of the samples fabricated from the same as-grown crystals as were used for the spectroscopic measurements were 0.45 at.%, which corresponds to $N = 2.5 \times 10^{19}$ ions cm⁻³. The prismatic samples used in the measurements were oriented by standard x-ray diffraction techniques, then cut along and perpendicular to the optical *c*-axis.

Polarized optical absorption spectra for the π -configuration ($c \parallel E, c \perp k$) and σ -configuration ($c \perp E, c \perp k$), as well as unpolarized spectra, were recorded using Specord M-40 (Carl Zeiss-Jena) and SF-8 (LOMO) spectrophotometers in the spectral region 0.350–2 μ m using a Glan–Thompson polarizer. Measurements were performed at 77 K and 300 K.

Lifetime measurements were carried out by using pulsed YAG:Nd laser second harmonics (0.53 and 0.66 μ m) with the pulse width of ~ 20 ns. The luminescence was analysed with an SDL-1 (LOMO) spectrometer, detected with an FD-10 photodiode, and recorded with an S1-75 oscilloscope.

3. Results and discussion

In order to determine the Stark sublevels of the ground $^4I_{15/2}$ and the $^4S_{3/2}$ multiplets of Er³⁺ ions in PbMoO₄ crystals, the optical absorption and photoluminescence spectra corresponding to $^4I_{15/2} \leftrightarrow ^4S_{3/2}$ transitions were recorded. Figure 1 shows the 77 K optical absorption spectra of the $^4I_{15/2} \rightarrow ^4S_{3/2}$ transition for two orientations of the optical *c*-axis with respect to the direction of the light propagation, and the energy level scheme of the $^4I_{15/2}$ and $^4S_{3/2}$ multiplets with corresponding optical transitions between them. The room temperature polarized optical absorption spectra used further for the Judd–Ofelt parameter calculation were recorded both parallel (π -spectrum) and perpendicular (σ -spectrum) to the optical *c*-axis. In the figure, for convenience of comparing transitions, the arrows in the scheme and the lines in the spectra are connected by common enumeration. The determination of the upper four Stark levels of the ground state $^4I_{15/2}$ (in the figure they are in brackets) was possible only from the room temperature absorption spectra and comparison with those obtained from luminescence spectra of this transition. The determination of the positions of the upper Stark levels of the ground state was complicated because of a strong broadening of the spectral lines. Therefore the levels which require improvement are marked with asterisks on the scheme and the Stark splittings of the lowest levels of the ground state $^4I_{15/2}$ are indicated by the square brackets on the spectra. The strong orientational dependence of the intensity of the spectral lines had motivated the spectroscopic investigation in the polarized light.

The energy of the Stark levels of the $^4I_{9/2}$ and $^4I_{11/2}$ multiplets was determined from the optical absorption spectra of the $^4I_{15/2} \rightarrow ^4I_{9/2}, ^4I_{11/2}$ transitions of the PbMoO₄:Er³⁺ crystals. Figure 2 and figure 3 show the 77 K orientation dependencies of the optical absorption spectra of the appropriate transitions, energy level schemes for the $^4I_{9/2}$ and $^4I_{11/2}$ multiplets and transitions between them, and also the 300 K polarized spectra for π - and σ -configurations necessary for the calculation of the Judd–Ofelt parameters. The labels are the same as in

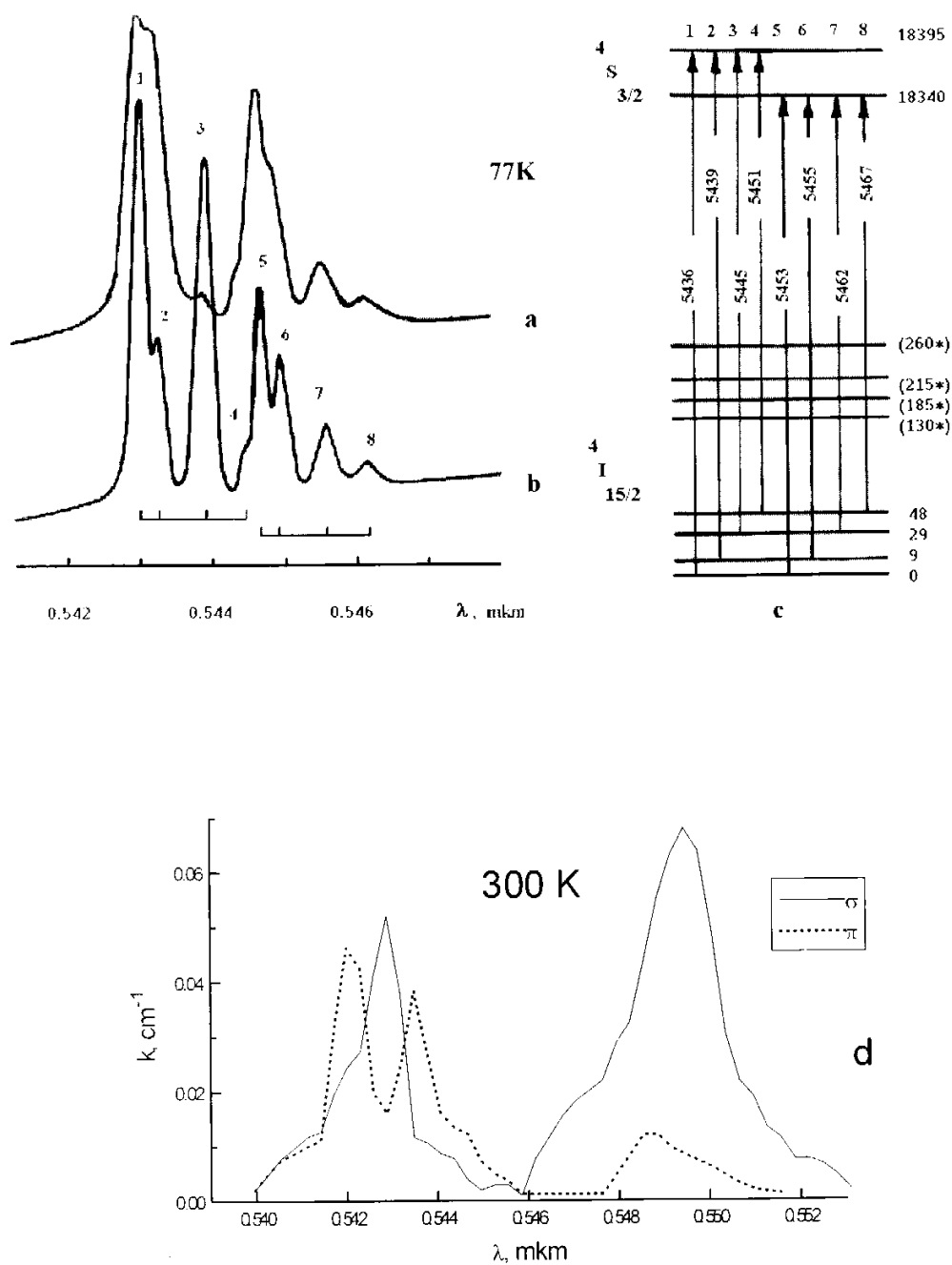


Figure 1. Optical absorption spectra (the $4I_{15/2} \rightarrow 4S_{3/2}$ transition) with unpolarized light propagating parallel (a) and perpendicular (b) to the optical *c*-axis of the crystal, and the energy level diagram (c) at 77 K, and with polarized light for the π -configuration ($c \parallel E, c \perp k$) and the σ -configuration ($c \perp E, c \perp k$) at 300 K (d). The level energy is given in cm^{-1} and the transitions between the levels in \AA .

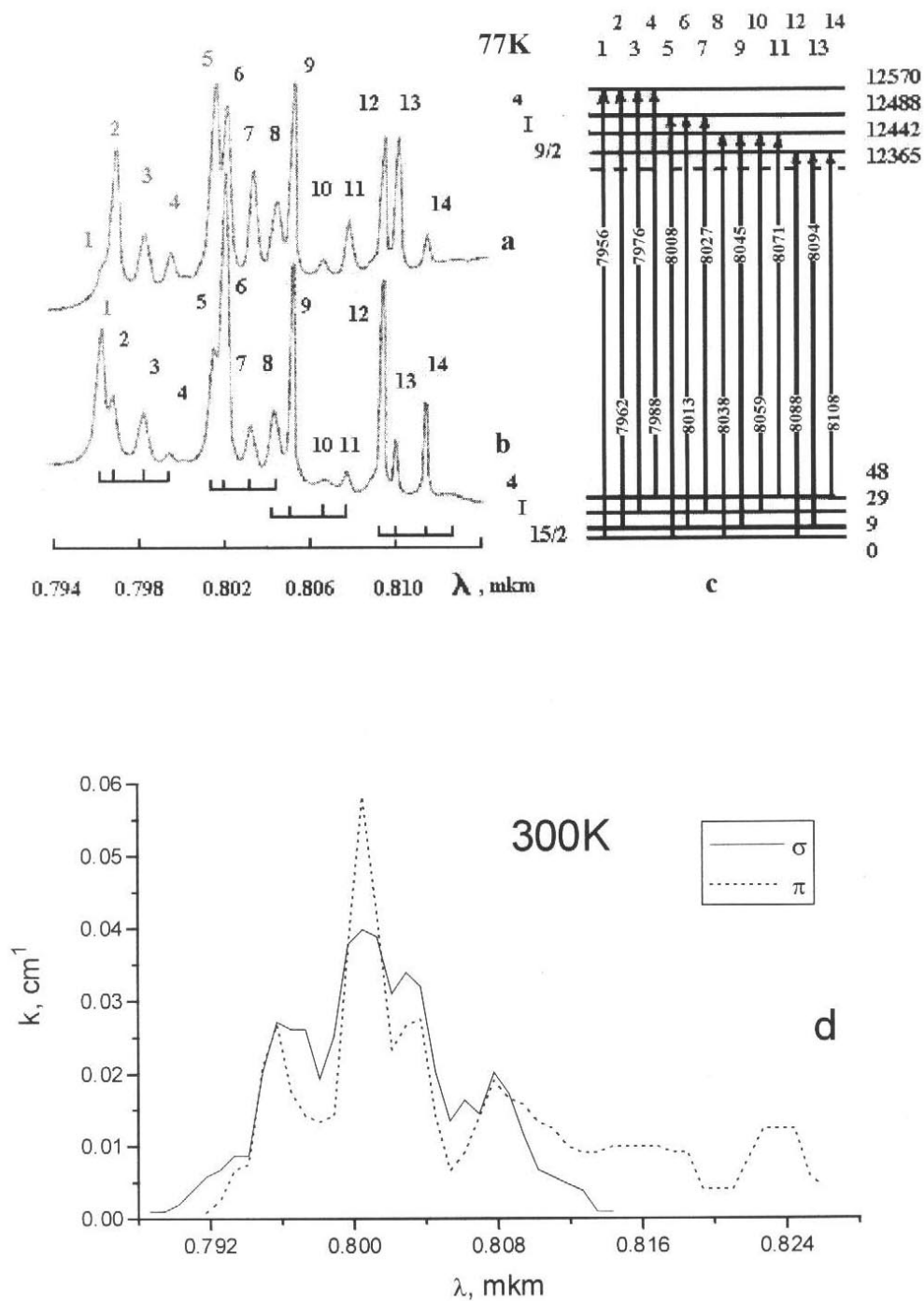


Figure 2. Optical absorption spectra (the $4I_{15/2} \rightarrow 4I_{9/2}$ transition) with unpolarized light propagating parallel (a) and perpendicular (b) to the optical c -axis of the crystal, and the energy level diagram (c) at 77 K, and with polarized light for the π -configuration ($c \parallel E, c \perp k$) and the σ -configuration ($c \perp E, c \perp k$) at 300 K (d). The notation is as for figure 1.

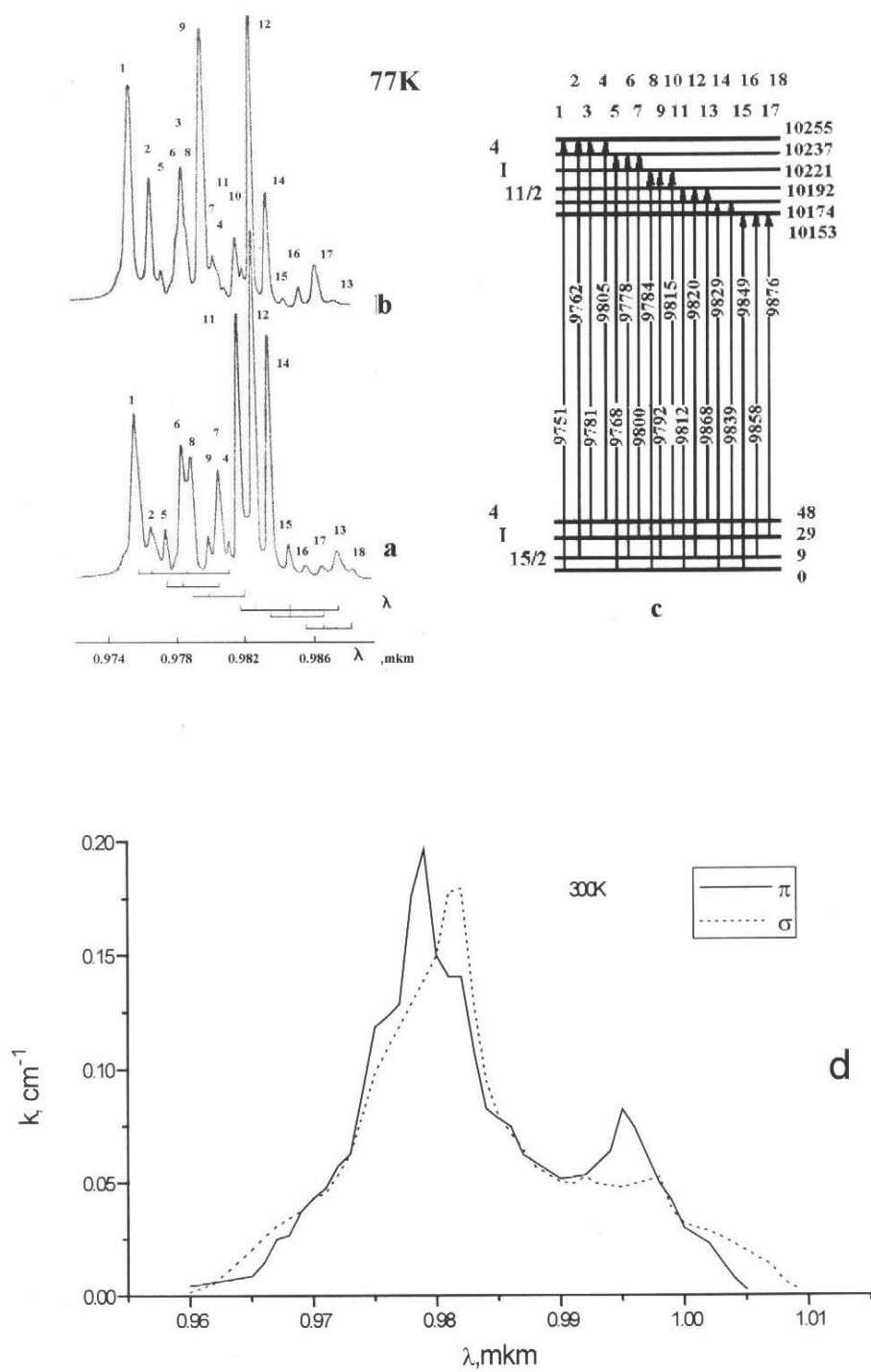


Figure 3. Optical absorption spectra (the $4I_{15/2} \rightarrow 4I_{11/2}$ transition) with unpolarized light propagating parallel (a) and perpendicular (b) to the optical c -axis of the crystal, and the energy level diagram (c) at 77 K, and with polarized light for the π -configuration ($c \parallel E$, $c \perp k$) and the σ -configuration ($c \perp E$, $c \perp k$) at 300 K (d). The notation is as for figure 1.

figure 1. The results obtained in the present work on the analysis of Stark levels of the Er^{3+} ions in PbMoO_4 crystals are in good agreement with similar data for the well-known laser crystals $\text{CaWO}_4:\text{Er}^{3+}$ [2] and $\text{LiYF}_4:\text{Er}^{3+}$ [3], which have similar crystal structure.

The strong σ - and π -polarized features of the absorption bands for Er^{3+} ions in PbMoO_4 crystals are illustrated in figure 4. It seems that it is necessary to apply a fully polarized Judd–Ofelt treatment for calculations of the radiative transition probability, taking into account such dependence. The number of observed multiplets is limited by the energy band gap—equal to about 3.3 eV for PbMoO_4 crystal [4]. Hence only eight optical absorption bands from the ground state $^4\text{I}_{15/2}$ of erbium ions in the total spectrum shown in figure 4 are explored. The experimental oscillator strengths, f_{exp} , of the $J \rightarrow J'$ transitions (J being the ground state $^4\text{I}_{15/2}$) are obtained from analysis of the $\int k(\lambda) d\lambda$ integral absorption coefficients of these eight bands using the following formula:

$$f_{J,J'} = (mc^2/\pi e^2 N \bar{\lambda}^2) \int k(\lambda) d\lambda \quad (1)$$

where m and e are the electron mass and charge respectively, c the speed of light in vacuum, $\bar{\lambda}$ the average wavelength of the $J \rightarrow J'$ transition, and N the erbium concentration.

On the other hand, the theoretical oscillator strengths, f_{th} , of the $J \rightarrow J'$ transitions are given by

$$f_{J,J'} = [8\pi^2 mc/3hn^2 \bar{\lambda} (2J+1)] [\chi^{ed} S^{ed} + \chi^{md} S^{md}] \quad (2)$$

where h is the Planck constant, n the refractive index of the host at the mean frequency of the transition, $\chi^{ed} = n(n^2+2)^2/9$ and $\chi^{md} = n^3$, S^{ed} and S^{md} are the line strengths for the electric dipole (ed) and magnetic dipole (md) transitions respectively. The refractive indices $n(\lambda)$ for ordinary and extraordinary waves of polarized light have been obtained from the Sellmeier equation for PbMoO_4 crystal reported in [5].

The line strength for the magnetic dipole transition between an initial state J and a final state J' is given by

$$S_{J,J'}^{md} = (h/4\pi mc)^2 |\langle 4f^N J || L + 2S || 4f^N J' \rangle|^2 \quad (3)$$

where $L + 2S$ is the magnetic dipole operator of the $J \rightarrow J'$ transitions. Because of the selection rules, the magnetic dipole transitions only contribute here to the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ absorption band. The values of S^{md} are usually small and are not sensitive to the host: we have used the values given in [6].

In the framework of the Judd–Ofelt theory [7, 8], the electric dipole line strengths are given by

$$S_{J,J'}^{ed} = \sum_{t=2,4,6} \Omega_t |\langle 4f^N J || U^{(t)} || 4f^N J' \rangle|^2 \quad (4)$$

where Ω_2 , Ω_4 , Ω_6 are the three intensity parameters (J–O parameters), which characterize the efficiency of interaction of the Er^{3+} ion with the field environment in PbMoO_4 crystal. It is known that the reduced matrix elements of the unit tensor operator $U^{(t)}$ ($t = 2, 4, 6$) are almost insensitive to the ion environment. They have been taken from [9] for the calculations. J–O parameters are found by least-squares fitting the measured f_{exp} -values given by (1) to the calculated ones, f_{th} , given by (2) taking into account (4). The aim of this procedure is to determine the parameters Ω_t for which the match of the experimental and theoretical values of the oscillator strengths is the best.

From the absorption spectra shown in figure 4, the experimental polarized oscillator strengths have been obtained. They are listed in table 1 along with the values fitted according

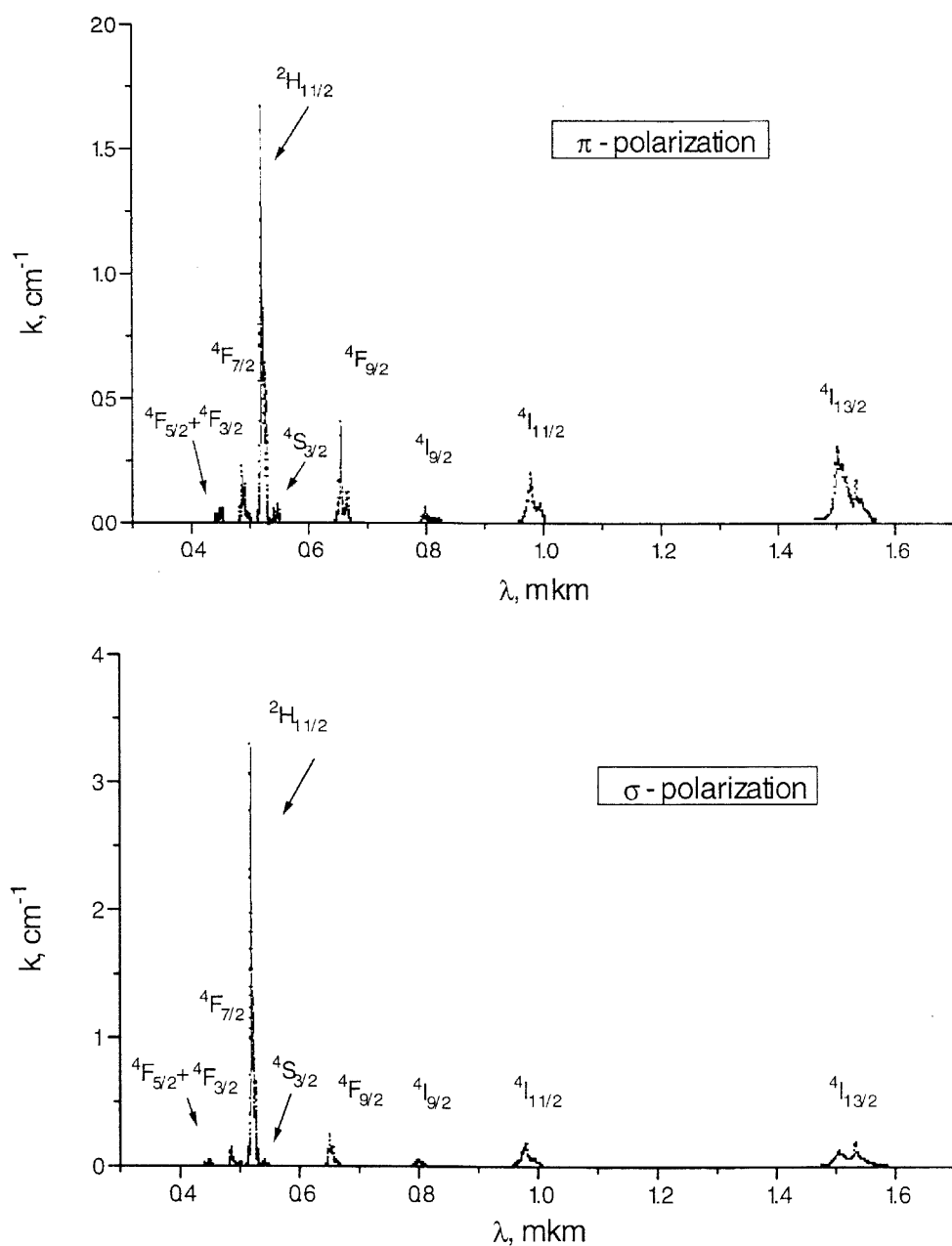


Figure 4. Total polarized absorption spectra of $\text{PbMoO}_4:\text{Er}^{3+}$ crystals at 300 K; π -polarization and σ -polarization.

to the Judd–Ofelt theory. Table 2 shows the Judd–Ofelt parameters that result from the above-mentioned analysis together with the effective Judd–Ofelt parameters $\Omega_i^{eff} = (2\Omega_i^\sigma + \Omega_i^\pi)/3$. A comparison of results of the Judd–Ofelt analysis carried out for polarized and unpolarized absorption spectra of noncubic crystals was given in [10], where for the best definition of the spectroscopic parameters of the crystals, polarized optical absorption spectra have been used.

Table 1. Polarized (π and σ) experimental and theoretical electric dipole oscillator strengths of Er^{3+} ions in PbMoO_4 crystal (md: magnetic dipole contribution; rms: root mean square value).

${}^4\text{I}_{15/2} \rightarrow J'$	π -polarization			σ -polarization		
	$10^{-6} f_{exp}^{ed}$	$10^{-6} f_{cal}^{ed}$	$10^{-6} \Delta f$	$10^{-6} f_{exp}^{ed}$	$10^{-6} f_{cal}^{ed}$	$10^{-6} \Delta f$
${}^4\text{I}_{13/2}$	$1.808 - 0.70^{md} = 1.108$	0.961	-0.147	$1.064 - 0.70^{md} = 0.364$	0.320	-0.034
${}^4\text{I}_{11/2}$	1.320	0.642	-0.678	1.312	0.368	-0.94
${}^4\text{I}_{9/2}$	0.346	0.296	-0.05	0.224	0.359	0.14
${}^4\text{F}_{9/2}$	1.974	1.864	-0.11	1.620	1.399	-0.22
${}^4\text{S}_{3/2}$	0.416	1.334	0.92	0.181	0.225	0.04
${}^2\text{H}_{11/2}$	13.061	13.099	0.038	17.297	17.276	-0.02
${}^4\text{F}_{7/2}$	2.288	2.647	0.359	1.337	1.009	0.33
${}^4\text{F}_{5/2} + {}^4\text{F}_{3/2}$	0.634	1.846	1.212	0.395	0.79	-0.02
	rms(Δf) = 0.77×10^{-6}			rms(Δf) = 0.46×10^{-6}		

Table 2. Comparison of the Judd–Ofelt parameters of Er^{3+} doped into some oxide laser crystals and into PbMoO_4 .

		Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)	Reference
PbMoO ₄	Ω_t^π	3.65	0.46	0.47	This work
	Ω_t^σ	4.32	0.53	0.07	
	Ω_t^{eff}	4.10	0.51	0.20	
YAG	—	0.66	0.81	0.71	[9]
YVO ₄	—	13.45	2.23	1.67	[12]
LiYF ₄	—	1.92	0.26	1.96	[13]
Y ₂ O ₃	—	4.59	1.21	0.48	[14]

In table 2 the J–O parameters for $\text{PbMoO}_4:\text{Er}^{3+}$ are compared with the values obtained for several laser crystals containing Er^{3+} . The parameter Ω_2 obtained in the present study is high, but it is lower than those for YVO_4 and Y_2O_3 . This possibly indicates that the polarizability of the ligand is high.

The total probabilities $A'_{JJ'}$ of spontaneous emission between the excited state J and the terminating state J' of the emission transitions $J \rightarrow J'$ are given by the expression

$$A_{JJ'} = A_{JJ'}^{ed} + A_{JJ'}^{md} = [64\pi^4 e^2 / 3h\bar{\lambda}^3 (2J + 1)] [\chi^{ed} S^{ed} + \chi^{md} S^{md}] \quad (5)$$

where $A_{JJ'}^{ed}$ and $A_{JJ'}^{md}$ are the spontaneous emission probabilities of the electric dipole (ed) and magnetic dipole (md) transitions respectively. The values of Ω_t^{eff} can now be used to calculate $A_{JJ'}^{ed}$ for any pair of multiplets of Er^{3+} ions using formula (4). To define $A_{JJ'}^{md}$ using formula (3), the matrix elements $|\langle ||L + 2S|| \rangle|^2$ of the magnetic dipole emission transitions $J \rightarrow J'$ and the wave functions of the Er^{3+} ion were taken from [9]. The values $\chi^{ed(md)}$ are taken as averages over π - and σ -polarizations: $\chi = (\chi_\pi + 2\chi_\sigma)/3$. The branching ratio for each emission from the same excited state J is represented by the equation

$$\beta_{JJ'} = A_{JJ'} / \sum_{J'} A_{JJ'}$$

and the radiative lifetimes τ_R are given by

$$\tau_R = \left(\sum_{J'} A_{JJ'} \right)^{-1}.$$

The calculated electric and magnetic dipole spontaneous emission probabilities for the main emission transitions of Er³⁺ ions in PbMoO₄, radiative lifetimes, and branching ratios are summarized in table 3. The average lifetimes τ_m of the metastable levels experimentally measured at room temperature by means of the decay of the luminescence are also included in the same table. Comparison of our results obtained by measuring the luminescence decay of excited Er³⁺ levels in PbMoO₄ with similar results given in [11] for the CdMoO₄:Er³⁺ crystal with the same structure shows that those values are of same order of magnitude. The conclusion reached by the authors in [11] that ~80% of the excitation energy transfers nonradiatively to the ⁴I_{13/2} multiplet, which decays only by emission, can be extended to PbMoO₄:Er³⁺. Therefore the values of $1/\tau_m$ for the ⁴S_{3/2}, ⁴F_{9/2}, and ⁴I_{11/2} multiplets are practically equal to the probabilities of nonradiative transitions from each of these multiplets to the lower-lying multiplet.

Table 3. Calculated electric dipole and magnetic dipole transition probabilities, radiative lifetimes, branching ratios, and experimental lifetimes for Er³⁺ ions in PbMoO₄ crystal.

$J \rightarrow J'$	λ (μm)	$\beta'_{JJ'}$	$A'_{JJ'}$ (s ⁻¹) (calculated)	τ_R (μs) (calculated)	τ_m (μs)
⁴ I _{13/2} → ⁴ I _{15/2}	1.52	1	78 + 113 ^{md}	5200	6500
⁴ I _{11/2} → ⁴ I _{15/2}	0.98	0.81	154	5300	400
⁴ I _{11/2} → ⁴ I _{13/2}	2.78	0.19	12 + 24 ^{md}		
⁴ I _{9/2} → ⁴ I _{15/2}	0.81	0.84	138	6100	—
⁴ I _{9/2} → ⁴ I _{13/2}	1.72	0.14	23		
⁴ I _{9/2} → ⁴ I _{11/2}	4.55	0.02	0.7+2.7 ^{md}		
⁴ F _{9/2} → ⁴ I _{15/2}	0.66	0.91	1379	660	~ 1.5
⁴ F _{9/2} → ⁴ I _{13/2}	1.17	0.05	79		
⁴ F _{9/2} → ⁴ I _{11/2}	2.02	0.04	56		
⁴ F _{9/2} → ⁴ I _{9/2}	3.64	0.01	7		
⁴ S _{3/2} → ⁴ I _{15/2}	0.55	0.70	785	900	16
⁴ S _{3/2} → ⁴ I _{13/2}	0.85	0.24	272		
⁴ S _{3/2} → ⁴ I _{11/2}	1.23	0.02	21		
⁴ S _{3/2} → ⁴ I _{9/2}	1.68	0.04	41		

4. Conclusions

Spectroscopic investigations of PbMoO₄:Er³⁺ crystals grown by the Czochralski technique have shown that they admit activation by erbium ions and have high optical quality. The optical absorption spectra exhibit a strong dependence of the absorption bands on the polarization. Therefore a fully polarized Judd–Ofelt treatment is required in order to calculate the experimental oscillator strengths. The spectroscopic characteristics obtained on the basis of the analysis of the optical polarized absorption spectra by using the Judd–Ofelt theory have shown that this crystal looks promising for laser applications in the IR region. The high rates of nonradiative relaxation from the excited states to the level ⁴I_{13/2} ensure its effective population. This allows us to conclude that there is a possibility of generation of stimulated emission based on the ⁴I_{13/2} → ⁴I_{15/2} transition.

Acknowledgments

We wish to thank Dr C Pedrini and Dr A Petrosyan for the chemical analysis of the samples investigated, carried out at the Central Service d'Analyse (Vernaison, France), and S Karagezyan for providing us with the $\text{PbMoO}_4:\text{Er}^{3+}$ crystals.

References

- [1] Aghamalyan N R, Karagezyan S M and Kostanyan R B 1993 *J. Contemp. Phys.* **28** 26
- [2] Wortman D E 1971 *J. Chem. Phys.* **54** 314
- [3] Petrov M V and Tkachuk A M 1978 *Russ. Opt. Spectrosc.* **45** 147
- [4] Mushinskii V P, Karaman M I and Makarenko A P 1988 *Russ. J. Appl. Spectrosc.* **48** 839
- [5] Coquin G A, Pinnow D A and Warner A W 1971 *J. Appl. Phys.* **42** 2162
- [6] Carnall W T, Fields P R and Rajnak K 1968 *J. Chem. Phys.* **49** 4412
- [7] Judd B R 1962 *Phys. Rev.* **127** 750
- [8] Ofelt G S 1962 *J. Chem. Phys.* **37** 511
- [9] Weber M J 1967 *Phys. Rev.* **157** 262
- [10] Nunez L, Lifante G and Cusso F 1996 *Appl. Phys. B* **65** 485
- [11] Reut E G and Ryskin A I 1973 *Phys. Status Solidi a* **7** 47
- [12] Ermeneux F S, Moncorge R, Kabro P, Capobianco J A, Bettinelli M and Cavalli E 1996 *OSA Trends Opt. Photon.* **1** 498
- [13] Tkachuk A M, Politimova A V and Petrov M V 1985 *Russ. Opt. Spectrosc.* **59** 1136
- [14] Krupke 1966 *Phys. Rev.* **145** 325