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Optical Absorption and Emission from Ho^{3+} Ions in $KCaF_3$ Crystals

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The optical absorption, emission, and excitation spectra are reported for $KCaF_3:Ho^{3+}$ crystals. The Ho^{3+} ions evidently occupy only one site in this lattice. The measured oscillator strengths for several transitions are compared with values calculated from Judd–Ofelt theory and the calculated radiative rates are also tabulated. The temperature dependence of the lifetimes suggests that energy transfer occurs between Ho^{3+} ions at concentration levels of 1.3 at.%. © 1988 Academic Press, Inc.

Introduction

Rare earth ions are excellent laser sources and many different crystals have been used to host the lanthanides. One extensively studied lanthanide ion is Ho^{3+}. Stimulated emission has been observed for at least 12 of the Ho^{3+} transitions in the wavelength range 0.55 to 3.91 μm in crystals (*1–7*), thin films (*8*), and glasses (*9, 10*). Lasers have been constructed using Ho^{3+} ion in several perovskite crystals (*6, 11–15*). The fluoride perovskites are of particular interest because the phonon energies are low. This suggests weak multiphonon emission and the possibility of high quantum efficiency. In this paper we report on the relative ease with which Ho^{3+} ions enter the $KCaF_3$ lattice and on the optical properties of Ho^{3+} in this fluoroperovskite crystal. Our results are compared with those reported for $LiHoF_4$ crystals (*16*) and fluorozirconate glass containing Ho^{3+} ions (*17*).

Experimental Procedure

Crystals of $KCaF_3$ with HoF_3 (2 at.%) added to the melt as impurity were grown by the Bridgeman technique at the Oklahoma State University Crystal Growth Facility. Optical absorption spectra were taken with a Perkin–Elmer 330 spectrophotometer at 300 and 77 K. Integrated intensities were calculated by numerical integration. The emission and excitation spectra of the sample were generated by excitation from appropriate chopped light from a 150-W xenon–arc lamp previously routed through a 0.22-m Spex double monochromator. The fluorescence was focused into a 0.8-m Spex monochromator and reflected to a cooled RCA C31034 photomultiplier tube (PMT) for visible detection or an Optoelectronics OTC-22-53 PbS cell for infrared detection. The signal from the detector was preamplified and passed through a

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lock-in amplifier whose reference was the variable-speed light chopper in the excitation beam. The output of the lock-in was stored in a Hewlett–Packard HP-87 microcomputer. A quartz iodine lamp traceable to the National Buearu of Standards was used to correct the monochromator and PMT response.

The intensity of the excitation light was measured with a Photo Research Model 310 photometer/radiometer and the excitation spectra were corrected accordingly. Lifetime measurements were made using a Nicholet 1070 signal averager. For low temperature measurements a liquid nitrogen cryostat or a CTI Cryodyne cryocooler Model 21 SC were utilized. The cryocooler has an incorporated resistance heater which allows temperature control within ±2 K over the range 14 to 300 K.

The holmium concentration was measured at Oak Ridge National Laboratory by inductively coupled plasma techniques to be 1.63 ± 0.01 weight%. The index of refraction for these crystals was measured by Dr. E. Arakawa at ORNL to be $n_1 = 1.409$ (400 nm), $n_2 = 1.395$ (700 nm), $n_3 = 1.399$ (1200 nm), $n_4 = 1.387$ (1900 nm).

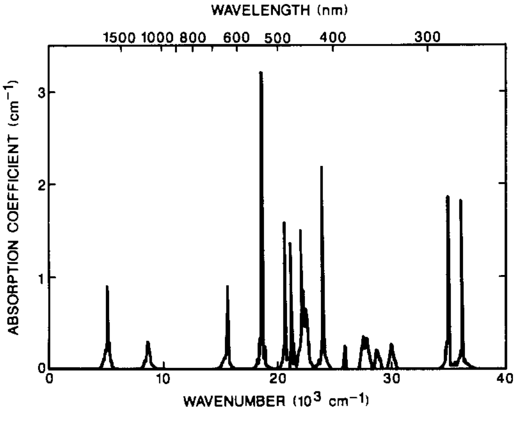

FIG. 1. Optical absorption spectrum of $KCaF_3 : Ho^{3+}$ at 77 K.

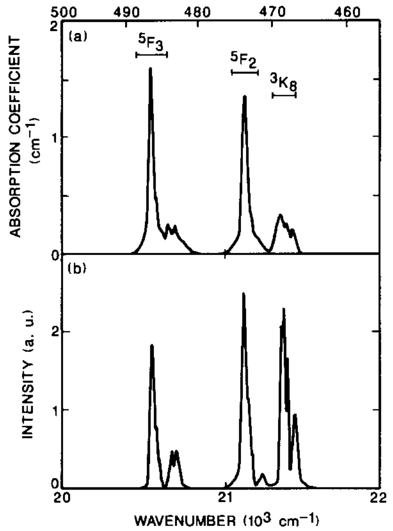

FIG. 2. Absorption (a) and excitation (b) spectra (monitored using the $^5S_2$ emission) showing the ground state transitions to the $^5F_3$, $^5F_2$, and $^3K_8$ levels of Ho^{3+} ions in $KCaF_3$ crystals.

Experimental Results

The optical absorption spectrum of $KCaF_3 : Ho^{3+}$ was taken at 300 and 77 K over the wavelength range 250 to 2500 nm. Figure 1 portrays the absorption spectrum at 77 K. High resolution excitation measurements were made at 14 K in order to determine the structure of the J-manifolds. The expanded absorption spectrum is displayed in Fig. 2a and the excitation spectrum for transitions from the ground state $^5I_8$ to the levels $^5F_3$, $^5F_2$, and $^3K_8$, is portrayed in Fig. 2b. The resolution in Fig. 2a is ~ 100 cm^{-1} and is much worse than for the data in Fig. 2b (~ 10 cm^{-1}). This explains the apparent differences in intensity. From these data it is possible to resolve the structure of the multiplets. The observed splittings are listed in Table I. Table I provides the energy levels of Ho^{3+} ions in $KCaF_3$ and $LiHoF_4$ (*16*). The energy level diagram for Ho^{3+} obtained from the data for energies up to 40,000 cm^{-1} is depicted in Fig. 3.

TABLE I

Energy Levels (cm^{-1}) for Ho^{3+}

	LiHoF$_4$		KCaF$_3$		LiHoF$_4$	KCaF$_3$		LiHoF$_4$		KCaF$_3$		LiHoF$_4$	KCaF$_3$
Level	Exp.	Calc.	Exp.	Level	Exp.	Exp.	Level	Exp.	Calc.	Exp.	Level	Exp.	Exp.
$^5I_8$	0	0	0	$^5S_2$	18,490	18,455		8,668	8,668			21,483	
	8	8	8		18,507	18,476			8,674	8,681		21,497	21,463
	26	20	45		18,511	18,524		8,735	8,733				
	49	50	68					8,749	8,749		$^5G_6$	22,137	22,014
	61	59		$^5F_4$	18,613	18,534		8,759	8,763			22,143	22,034
	78	72	121		18,621	18,556						22,156	22,071
		211	146		18,689	18,565	$^5I_5$	11,219	11,211			22,247	22,101
		273			18,689–18,720	18,582			11,215			22,297	22,138
		275			18,717	18,597			11,219			22,316	22,156
		284	178			18,635		11,227	11,221			22,362	22,317
		294	204			18,677		11,228	11,227			22,381	22,348
		296	306					11,278	11,279			22,393–22,466	22,467–22,512
		310	349	$^5F_3$	20,632	20,570		11,304	11,313				
					20,638	20,588		11,310	11,323		$^5F_1$	22,466	22,512
$^5I_7$	5,146	5,145	4,926		20,650	20,684	$^5I_4$	13,185	13,184		$^5G_5$	23,982	23,908
	5,148	5,151			20,667	20,699		13,260	13,258			23,989	23,962
	5,154	5,156			20,710			13,321	13,320			23,997	
		5,161			20,757				13,324			24,005	
	5,177	5,178			20,768	20,724			13,329			24,029	
	5,200	5,198	5,097					13,520	13,391			24,081	24,076
	5,221	5,221		$^5F_2$	21,140	21,143			13,510			24,087	
	5,225	5,227			21,187	21,170						24,092	
	5,281	5,281	5,160		21,216	21,263	$^5F_5$	15,485		15,119		24,124	24,166
	5,285	5,284						15,495		15,209		24,158	24,192
	5,291	5,285	5,291	$^3K_8$	21,371	21,388		15,505		15,373		24,224	
					21,380			15,550		15,601			
$^5I_6$	8,644	8,640			21,390	21,398		15,605–15,700		15,647	$^5G_4$	25,908	
	8,650	8,648			21,400			15,630–16,640		15,674		25,959	25,934
	8,656	8,655			21,418	21,420				15,699		25,978	25,975
		8,656	8,347		21,453							26,018	26,005
	8,657	8,655			21,473							26,067	26,208

Note. Data for LiHoF$_4$ are taken from Ref. (*10*).

The lifetime of the $^5S_2$ ($^5F_4$) emission to the ground state was measured as a function of temperature. The results are displayed in Fig. 4. The lifetimes for the infrared transitions are 5 msec for the $^5I_7 \rightarrow {}^5I_8$ at 10 K and 3 msec at 298 K. For the $^5I_6 \rightarrow {}^5I_8$ transition the lifetimes are 7.5 msec at 10 K and 4.5 msec at 298 K.

Discussion

From the excitation spectra in Fig. 2, it is evident there are 5, 3, and 4 lines for the $^5F_3$, $^5F_2$, and $^3K_8$ transitions, respectively. Group theory predicts that the total number of lines should be 5, 4, and 13 lines for ions in a single site of less than cubic symmetry. Since for both absorption and excitation no extra sets of lines for any *J*-manifold are observed we believe that the Ho^{3+} ions occupy only one site in the host. If this is correct this material could be important in the search for new laser systems since there would be one active site and since ions are so easily incorporated in the lattice. For example, 65% of the impurity ions in the starting material entered the crystal. Therefore, an evaluation of the oscillator strengths and branching ratios will be useful for further work.

The Judd–Ofelt theory can be applied to holmium-doped KCaF$_3$ to determine the strengths of the absorption transitions observed at room temperature. These can be

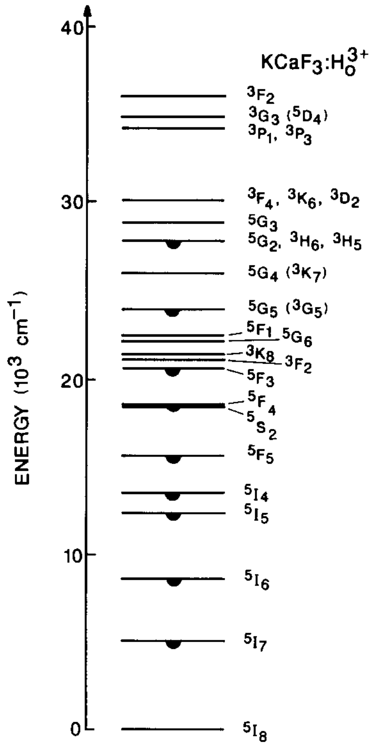

FIG. 3. Energy level diagram of Ho^{3+}. The half circles indicate the levels from which emission is relatively intense.

TABLE II

MEASURED OSCILLATOR STRENGTHS OF Ho^{3+} IN SEVERAL HOSTS AT 300 K

Level	Oscillator strength (10^{-8})			
	$KCaF_3$	LaF_3[a]	$YA10_3$[a]	ZBLA[b]
$^5I_7$	79.1	68.0	128.0	144.0
$^5I_6$	51.0 (49)	36.0	64.0	72.0
$^5I_5$	—	6.2	12.0	11.6
$^5I_4$	—	—	4.0	1.5
$^5F_5$	105.4 (120)	131.0	217.0	267.4
$^5S_2$, $^5F_4$	168.9 (168)	140.0	270.0	355.4
$^5F_3$	40.0 (55)	93	65.0	235.8
$^5F_2$	40.4 (31)		39.0	
$^3K_8$	18.0 (33)		70.0	
$^5G_6$	278.2 (278)	435.0	745.0	1045.6
$^5G_5$	102.9 (46)	110.0	210.0	231.9
$^5G_4$, $^3K_7$	24.6 (22)	21.0	51.0	47.4
$^5G_2$, $^3H_5$, $^3H_6$	97.5 (99)	148.0	252.0	337.1
$^3G_3$, $^5D_4$	93.0 (92)	120.0	242.0	273.5
$^3F_2$, $^3H_4$	78.0 (80)	106.0	173.0	215.0

Note. The transitions are all from the $^5I_8$ ground level to the level indicated. The numbers in parentheses for $KCaF_3$ are the calculated values from Judd–Ofelt.

[a] Ref. (*24*).

[b] Ref. (*17*).

calculated from the following equation:

$$f = \frac{mcn^2}{\pi e^2 NX} \int \alpha(\nu)d\nu, \qquad (1)$$

where e and m are the electronic charge and mass, c is the velocity of light, n is the refractive index of the crystal, $N = 1.6 \times 10^{20}$ cm^{-3} is the number of absorbing ions per cm^3, and α is the absorption coefficient. The X term is the effective field correction for a well-localized center in a medium of isotropic refractive index n. For electric dipole transitions X is given by $X_{ED} = n(n^2 + 2)^2/9$, while for magnetic dipole transitions it is $X_{MD} = n^3$. As noted earlier the refractive index was measured in the range 400 to 1900 nm at Oak Ridge National Laboratory as was the concentration of holmium.

The oscillator strengths obtained from Eq. (1) are tabulated in Table II and compared with those for other host materials. In the Judd–Ofelt theory (*18, 19*) the electric dipole oscillator strength for a transi-

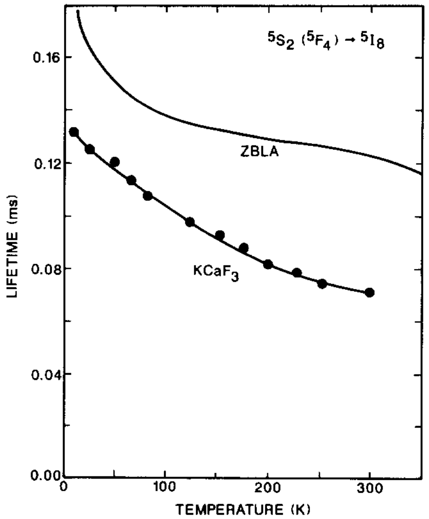

FIG. 4. The temperature dependence of the lifetimes for the $^5S_2(^5F_4) \rightarrow {}^5I_8$ transition in ZBLA glass (*17*) and $KCaF_3$ crystals.

tion from J to J' at an average frequency $\bar{\nu}$ is

$$f(a, J; b, J') = \frac{8\pi^2 m\bar{\nu}}{3h(2J+1)e^2} S_{\mathrm{ED}}(a, J; b, J'), \quad (2)$$

where S_{ED} is the electric dipole line strength,

$$S_{\mathrm{ED}} = e^2 \sum_{t=2,4,6} \Omega_t(\langle f^N J \| u^{(t)} \| f^N J' \rangle)^2, \quad (3)$$

and the squared terms are the reduced matrix elements of the tensor operators $U^{(t)}$ (*20, 21*). These matrix elements have been tabulated for many different ions and have been found to be almost invariant from host to host (*22, 23*). For the present work the values calculated by Weber (*24*) and Carnall (*25*) were utilized. The Ω_t parameters defined in Eq. (3) are phenomenological parameters obtained through experimentally determined oscillator strengths. These values are determined by a least-square fitting procedure. The parameters are $\Omega_2 = 0.51 \times 10^{-20}$ cm^2, $\Omega_4 = 1.22 \times 10^{-20}$ cm^2, and $\Omega_6 = 1.20 \times 10^{-20}$ cm^2. From these values the oscillator strengths are calculated and are presented in Table II. The quality of the fit can be estimated through the root mean square deviation of the measured and calculated line strengths. The rms deviation was 2.12×10^{-7}.

The spontaneous emission probability A for excited states and for forced electric dipole transitions for excited states were calculated from the expression:

$$A_{\mathrm{ED}}(a, J; b, J') = \frac{64\pi^4\bar{\nu}^3}{3(2J+1)hc^3}\frac{n(n^2+2)^2}{9} S_{\mathrm{ED}}. \quad (4)$$

From these values the radiative lifetime τ_{R} of an excited state i is found to be:

$$\frac{1}{\tau_{\mathrm{R}_i}} = \sum_j A(i, j), \quad (5)$$

where the summation is carried over electric and magnetic dipole transitions of all terminal states j and the branching ratio is given by:

$$\beta_{ij} = \frac{A(i, j)}{\sum_j A(i, j)} = \tau_{\mathrm{R}_i} A(i, j). \quad (6)$$

The calculated values for A, τ, and β for several states are given in Table III. For the $^5I_7 \rightarrow {}^5I_8$ transition the total spontaneous probability (electric plus magnetic dipole) was found to be $42s^{-1}$ through the relation (*26, 27*):

$$A(a, J; bJ') = \frac{8\pi n^2\bar{\nu}^2}{Nc^2}\frac{2J'+1}{2J+1}\int \alpha(\nu)d\nu. \quad (7)$$

Table IV provides the Ω_t values for Ho^{3+} in several different materials. The lower Ω_2 value for KCaF$_3$:Ho suggests that in this host the Ho^{3+} ions are in sites with a symmetry close to cubic. Charge compensation is necessary and the Ho^{3+} ions enter the lattice either as pairs or compensated by a nearby vacancy. If the Ho^{3+} ions are paired this would explain the effective energy transfer as suggested by the temperature dependence and the magnitude of the lifetimes (Fig. 4). There is, of course, considerable evidence that trivalent ions do enter this type of lattice as pairs (*28–31*) and that energy transfer is relatively efficient. On the other hand, for this lattice structure Kay and McPherson (*32*) found Cr^{3+} ions substituting for divalent host ions were compensated by alkali metal ion vacancies. Other investigators have also obtained evidence for this type of compensation (*33–35*).

Summary

1. Rare earth impurity ions readily enter KCaF$_3$ with 65% of the ions in the melt being incorporated in the crystal.

2. The Ho^{3+} ions apparently substitute

TABLE III

PREDICTED SPONTANEOUS EMISSION PROBABILITIES AND BRANCHING RATIOS OF Ho^{3+} IN $KCaF_3$ FOR SELECTED TRANSITIONS

Transitions	Average frequency (cm^{-1})	A_{ED} (sec^{-1})	τ_R (msec)	Branching ratios
$^5I_7 \rightarrow {}^5I_8$	5,123	30.8		1.00
$^5I_6 \rightarrow {}^5I_8$	8,661	78.0	11.7	0.91
$^5I_7$	3,538	7.6		0.09
$^5I_5 \rightarrow {}^5I_8$	12,366	37.3	9.0	0.34
$^5I_7$	7,246	66.1		0.60
$^5I_6$	3,708	7.3		0.07
$^5I_4 \rightarrow {}^5I_8$	13,558	4.5	21.7	0.10
$^5I_7$	8,435	22.6		0.49
$^5I_6$	4,897	18.6		0.40
$^5I_5$	1,190	0.4		0.01
$^5F_5 \rightarrow {}^5I_8$	15,601	722.2	1.1	0.78
$^5I_7$	10,434	167.8		0.18
$^5I_6$	6,896	39.0		0.04
$^5I_5$	3,189	1.2		0
$^5I_4$	1,999	0		0
$^5S_2 \rightarrow {}^5I_8$	18,469	622.7	0.9	0.54
$^5I_7$	13,346	420.0		0.37
$^5I_6$	9,808	72.1		0.06
$^5I_5$	6,100	11.2		0.01
$^5I_4$	4,910	16.2		0.01
$^5F_5$	2,868	0.2		0
$^5F_4 \rightarrow {}^5I_8$	18,621	1450.9	0.6	0.84
$^5I_7$	13,498	133.6		0.08
$^5I_6$	9,960	98.9		0.06
$^5I_5$	6,253	33.8		0.02
$^5I_4$	5,063	8.3		0
$^5F_5$	3,021	1.2		0
$^5F_3 \rightarrow {}^5I_8$	20,580	925.3	0.6	0.52
$^5I_7$	15,457	529.9		0.32
$^5I_6$	11,919	156.0		0.09
$^5I_5$	8,211	0		0
$^5I_4$	7,021	51.1		0.03
$^5F_5$	4,979	6.7		0
$^5S_2$	2,111	0		0
$^5F_4$	1,959	0.4		0
$^5G_6 \rightarrow {}^5I_8$	22,150	2857.6	0.3	0.80
$^5I_7$	17,027	611.2		0.17
$^5I_6$	13,489	77.6		0.02
$^5I_5$	9,781	0		0
$^5I_4$	8,592	0.2		0
$^5F_5$	6,549	39.5		0.01
$^5S_2$	3,681	2.3		0
$^5F_4$	3,529	3.4		0
$^5F_3$	1,570	0.1		0
$^3F_2$	1,011	0		0
$^3K_8$	760	0		0
$^5G_5 \rightarrow {}^5I_8$	23,950	669.9	0.7	0.47
$^5I_7$	18,827	488.9		0.34
$^5I_6$	15,289	208.5		0.15
$^5I_5$	11,581	0		0
$^5I_4$	10,391	10.9		0.01
$^5F_5$	8,349	33.1		0.02
$^5S_2$	5,481	3.1		0
$^5F_4$	5,328	8.0		0
$^5F_3$	3,370	1.5		0
$^3F_2$	2,810	0.7		0
$^3K_8$	2,560	0		0
$^5G_6$	1,800	0.6		0

for Ca^{2+} ions. Only one type of site is observed.

3. At an impurity level of $N = 1.6 \times 10^{20}\ cm^{-3}$ (1.3 at.%) energy transfer is dominant.

4. The calculated branching ratios suggest a number of laser transitions are possible.

TABLE IV

INTENSITY JUDD–OFELT PARAMETERS OF Ho^{3+} IN VARIOUS HOSTS

	$KCaF_3$	LaF_3[a]	$YA10_3$[a]	ZBLA[b]
$\Omega 2(10^{-20}\ cm^2)$	0.51	1.16	1.82	2.28
$\Omega 4(10^{-20}\ cm^2)$	1.22	1.38	2.38	2.08
$\Omega 6(10^{-20}\ cm^2)$	1.20	0.88	1.53	1.73

[a] Ref. (*24*).

[b] Ref. (*17*).

Acknowledgment

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References

1. L. F. Johnson and H. J. Guggenheim, *Appl. Phys. Lett.* **19,** 44 (1971).
2. Y. U. K. Voronko, A. A. Kaminskii, V. V. Osiko, and A. M. Prokhorov, *JETP Lett.* **1,** 3 (1965).
3. L. F. Johnson and H. J. Guggenheim, *IEEE J. Quantum Electron.* **10,** 442 (1974).
4. A. M. Morozov, I. G. Pogkolosina, A. M. Tkachuk, V. A. Fedorov, and P. P. Feofilov, *Opt. Spectrosc.* **39,** 338 (1975).
5. A. A. Kaminskii, T. I. Butaeva, A. D. Ivanov, I. V. Mochalov, A. G. Petrosyan, G. I. Rogov, and V. A. Fedorov, *Sov. Tech. Phys. Lett.* **2,** 308 (1976).
6. A. A. Kaminskii, A. O. Juanov, S. E. Sarkisov, I. V. Mochalov, J. A. Fedorov, and L. Li, *Sov. Phys. JETP* **44,** 516 (1976).
7. I. G. Podkolozina, A. M. Tkachuk, V. A. Fedorov, and P. P. Feofilov, *Opt. Spectrosc.* **40,** 111 (1976).
8. J. P. Van der Ziel, W. A. Bonner, L. Kopf, S. Singh, and L. G. Van Uitert, *Appl. Phys. Lett.* **22,** 656 (1973).
9. H. W. Gandy, R. J. Ginther, and J. F. Weller, *Appl. Phys. Lett.* **6,** 237 (1965).
10. M. Eyal, R. Reisfeld, C. K. Jorgenson, and B. Bendow, *Chem. Phys. Lett.* **126,** 181 (1986).
11. L. F. Johnson and A. A. Ballmen, *J. Appl. Phys.* **40,** 297 (1965).
12. J. A. Caird and L. G. DeShazer, *IEEE J. Quantum Electron.* **11,** 97 (1975).
13. H. V. Laver and F. K. Fong, *J. Chem. Phys.* **60,** 274 (1974).
14. A. A. Kaminskii, V. A. Fedorov, A. G. Petrosyan, A. A. Pavlyok, J. Bohm, P. Reiche, and D. Schultz, *Inorg. Mater.* **15,** 1180 (1979).
15. P. A. Arsenev and K. E. Bienert, *Phys. Status Solidi (A)* **13,** K129 (1972).
16. H. P. Christensen, *Phys. Rev. B* **19,** 6564 (1979).
17. K. Tanimura, M. D. Shinn, W. A. Sibley, M. G. Drexhage, and R. N. Brown, *Phys. Rev. B* **30,** 2429 (1984).
18. B. R. Judd, *Phys. Rev.* **127,** 750 (1962).
19. G. S. Ofelt, *J. Chem. Phys.* **37,** 511 (1962).
20. C. W. Nielson and G. F. Koster, "Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations." MIT Press, Cambridge, MA (1964).
21. B. G. Wybourne, "Spectroscopic Properties of Rare Earth Ions." Interscience, New York (1965).
22. R. Reisfeld, L. Boehm, N. Lieblich, and B. Barnett, *Proc. Tenth Rare Earth Conf.* **2,** 1142 (1973).
23. L. A. Riseberg and M. J. Weber, "Progress in Optics" (E. Wolf, Ed.), Vol. 14, p. 89. Elsvier, New York (1976).
24. M. J. Weber, B. H. Matsinger, V. L. Donlan, and G. T. Surrati, *J. Chem. Phys.* **57,** 562 (1972).
25. W. T. Carnall, "Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in LaF_3," Argonne National Laboratory.
26. M. J. Weber, T. E. Varitmos, and B. H. Matsinger, *Phys. Rev. B* **8,** 47 (1973).
27. W. F. Krupke, *IEEE J. Quantum Electron.* **10,** 450 (1974).
28. M. Arakawa, H. Ibisu, and H. Takeuchi, *J. Phys. Soc. Japan* **54,** 3577 (1985); **53,** 376 (1984).
29. G. L. McPherson and L. M. Henling, *Phys. Rev. B* **16,** 18,889 (1977).
30. A. M. McPherson and G. L. McPherson, *Solid State Commun.* **37,** 501 (1981).
31. P. A. M. Berdowski, M. J. J. Lammers, and G. Blasse, *J. Chem. Phys.* **83,** 476 (1985).
32. D. Kay and G. L. McPherson, *J. Phys. C.* **14,** 3247 (1981).
33. A. E. Usachev and Y. V. Yablokov, *Sov. Phys. Solid State* **24,** 852 (1982).
34. Y. Vaills and J. Y. Buzare, *J. Phys. C.* **20,** 2149 (1984).
35. J. Hutton and R. J. Nelms, *J. Phys. C.* **14,** 1713 (1981).