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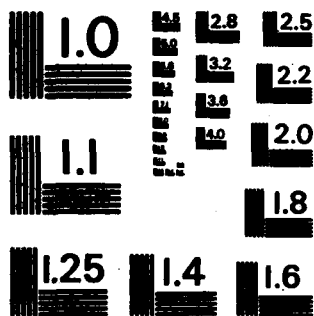
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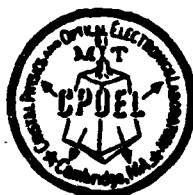
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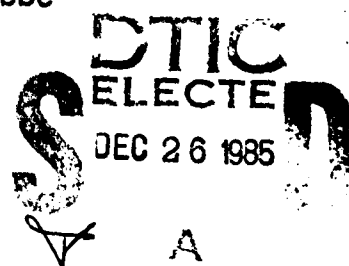
BaY_2F_8 AS A HOST FOR Ln IONS - OPTICAL
PROPERTIES OF THE CRYSTAL AND SPECTRO-
SCOPIC RESULTS FOR Pr, Dy, Ho, AND Er
DOPING.

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BAY₂F₈ AS A HOST FOR LN IONS. I: OPTICAL PROPERTIES OF THE CRYSTAL AND SPECTROSCOPIC RESULTS FOR Pr, Dy, Ho, AND Er DOPING.

H.P. Christensen, H.P. Jenssen, and D.R. Gabbe

micron

The three refractive indices for the monoclinic crystal BaY₂F₈ have been measured as function of the wavelength from 275 nm to 2.65 μ m, and the position of the index ellipsoid has been determined. Most energy levels with energy less than 25,000 cm⁻¹ have been determined from low-temperature spectroscopic data for Pr⁽³⁺⁾, Dy⁽³⁺⁾, Ho⁽³⁺⁾, and Er⁽³⁺⁾ in this structure. Further, the room-temperature fluorescence lifetimes have been measured for some of the multiplets of these four doping ions.

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I INTRODUCTION

BaY_2F_8 is an interesting host crystal for rare-earth ions. The compound was first observed in the complicated $\text{BaF}_2\text{-YF}_3$ phase diagram in 1967 by Ippolitov et al.¹. Since then several quantum-electronic processes have been described for rare-earth ions in this structure. Johnson and Guggenheim have reported laser action for $\text{Er}^{2,3}$, Dy^4 , and Ho^5 . The crystal is especially interesting in the infrared wavelength region due to the weak phonon activity - i.e. slow multiphonon relaxation. Lasing at 3 μm has been obtained for both Dy^4 and a Ho down-conversion laser⁶. Infrared to visible up conversion has been achieved for Yb-Er systems^{2,7}. Ultraviolet to visible energy transfer has also been reported for systems codoped with Eu^{2+} and a Ln^{3+} ion⁸.

Besides these applications little has been published about the properties of rare-earth doped BaY_2F_8 crystals. The purpose of this series of papers is to investigate some general properties of the crystal and the behaviour of Ln^{3+} ions in this structure in order to get a better understanding of these systems. In this first paper the optical properties of the undoped crystal are given for wavelengths from the ultraviolet to the infrared. The energy levels below 25 000 cm^{-1} are listed and discussed for the four doping ions Pr, Dy, Ho, and Er. Fluorescence lifetimes are also given for some of the multiplets of these ions.

II The BaY_2F_8 crystal structure

BaY_2F_8 single crystals belong to the monoclinic space group

C_{2h}^3 (C2/m)⁹⁻¹². The lattice constants are^{10,12}: $a = 697.2$ pm, $b = 1050$ pm, $c = 426.0$ pm, and $\beta = 99.7^\circ$. Each unit cell contains two BaY_2F_8 formula units. The point symmetries at the different sites are⁹: Two Ba sites with C_{2h} symmetry, four Y sites and four F sites with C_2 symmetry, four F sites with C_s symmetry, and eight F ions at general sites. Each Y ion is surrounded by eight F ions.

A Crystal growth

The samples used for the experiments were cut from large crystals of good optical quality. The crystals were grown by the Czochralski method in an argon atmosphere. The pulling was controlled by a mini computer, and smooth cylindrical rods with a diameter of approximately 2 cm were obtained. Due to nonuniform thermal expansion during cooling the crystals cleave easily after the growth. Purified starting materials were used, but still very weak fluorescence from several rare-earth ions could be seen even in the undoped crystal.

B Index of refraction

BaY_2F_8 has good optical properties. In addition to the excellent infrared behaviour, (infrared absorption edge at 9 μm) the crystal is transparent through the visible to beyond 200 nm in the ultraviolet. As a biaxial crystal three refractive indices are needed to describe the dielectric properties of BaY_2F_8 . The refractive indices have been measured as function of the wavelength in the spectral region 275 nm - 2.65 μm by the method described by Bond¹³. This method gives in addition to the numerical values of the indices the direction of the main axes x, y, and z of the index ellipsoid with re-

spect to the crystallographic axes a , b , and c as shown in figure 1. The obtained values for the indices and the angle ρ between the c and z axes are given in table I. and figure 2. Determination of ρ by this method gives poor accuracy unless the angle is large. Visual inspection between crossed polarizers gives a value for ρ around 23° .

C Micro hardness

The surface hardness of the crystal was measured with an "LL" Tukon Microhardness Tester, and the results are given in table II. On the Mohs scale the hardness corresponds to a value close to 5.

III SPECTROSCOPIC RESULTS

Trivalent rare-earth ions enter the Y sites¹⁴ in BaY_2F_8 substitutionally. The symmetry at this site is so low that the crystal field totally lifts the degeneracy of the multiplets for ions with an even number of electrons. For ions with an odd number of electrons all levels are doublets. The overall symmetry of the crystal makes six different polarized optical spectra possible. If only electric-dipole transitions are important, only three different spectra will be observed. For ions with an odd number of electrons there are no selection rules for transition probabilities. For ions with an even number of electrons the energy levels are separated into two sets, and transitions of electric-dipole nature between two levels of the same set are seen only for $E \parallel b$, whereas transitions between levels of different sets are seen only for $E \perp b$.

The energy levels were determined from absorption

5
and emission spectra at 10 K and slightly higher temperatures. A CARY 17DX instrument was used for absorption measurements. The emission spectra were obtained with a computer-controlled set up with a 1/3 meter McPherson monochromator and an argon laser for excitation. Polarized spectra were recorded for the ions with an even number of electrons. The fluorescence lifetimes were determined at room temperature. A pulsed dye laser was used for excitation. Lifetimes longer than 100 μ s were processed in a TMC computer of average transients. Shorter lifetimes were measured directly from the screen of a storage oscilloscope.

A Praseodymium

Most of the energy levels of the ground configuration of Pr^{3+} in BaY_2F_8 have been determined and are listed in table III. Energy levels have been obtained for all multiplets except $^1\text{S}_0$, where the only level is very high in energy. For five multiplets ($^3\text{P}_2$, $^3\text{P}_0$, $^1\text{D}_2$, $^3\text{F}_4$, and $^3\text{F}_2$) all levels have been determined, whereas some are missing for the remaining multiplets, of which most have high J numbers and therefore many levels. It has not been possible to separate $^1\text{I}_6$ and $^3\text{P}_1$. Transitions to the upper levels of several multiplets were phonon broadened prohibiting an exact determination of the energy of these levels. The accuracy on the levels of $^1\text{G}_4$ is also less than for the other levels, since absorption to this multiplet is very weak.

Polarized spectra were recorded only in absorption, so it has not been possible to give a symmetry assignment to those few levels involved only in emission - i.e. some levels of the ^3H multiplets. For absorption to $^3\text{F}_4$ and $^3\text{F}_3$

magnetic-dipole transitions are allowed since $\Delta J = 0$ and 1, respectively, and all transitions could be allowed in all polarizations, but the electric-dipole selection rules seem to be valid, and the assignments were made on the basis of these. A few extra lines were seen in the spectra, but they may be due to other impurities, although both absorption and emission measurements indicated a level at 5049 cm^{-1} .

Only the lifetime of the 3P_0 multiplet has been determined and is given in table VII.

B Dysprosium

All energy levels below $25\,000 \text{ cm}^{-1}$ except the one of $^6F_{1/2}$ and two of the ground multiplet $^6H_{15/2}$ have been determined for Dy^{3+} in BaY_2F_8 and are listed in table IV. The agreement with the energy levels reported by Johnson and Guggenheim⁴ is good, although there are a few significant differences. They report levels of the ground multiplet at 39.5 cm^{-1} and 590 cm^{-1} . Although two levels of $^6H_{15/2}$ are missing in our scheme, it is very unlikely that one of these should be at 39.5 cm^{-1} . Both should probably be found at energies higher than 200 cm^{-1} , since phonon activity, as for Pr^{3+} , smears out transitions to the upper levels of some multiplets. $^6F_{1/2}$ is not seen, since transitions from the ground multiplet to this level are strictly forbidden because $\Delta J > 6$. The accuracy of the levels of the three upper multiplets is less than for the other multiplets, since it was not possible at these wavelengths to resolve the weak transitions from the two lowest levels of the ground multiplet.

Only the lifetimes of the $^4F_{9/2}$ and $^6H_{13/2}$ multiplets have been measured at room temperature. The lifetime of $^6H_{13/2}$

was also measured at 77 K. The measured values are given in table VII as are values reported earlier by Johnson and Guggenheim⁴. The agreement is within experimental accuracy.

C Holmium

The large number of levels in many of the multiplets of Ho^{3+} prevented a complete determination of the energy levels of the lowest multiplets for this ion in BaY_2F_8 . Those levels obtained are listed in table V. Johnson and Guggenheim⁵ report some energy levels of four multiplets. The agreement with our results is rather good except for the ground multiplet, where they have a level at 20 cm^{-1} , which we do not see at all. Kurkin et al.¹⁴ have determined a level at 0.24 cm^{-1} from ESR spectra. Polarized absorption spectra are of little value, since the two levels of the ground state quasi doublet belong to different symmetry sets. Polarized emission spectra are also difficult to explain due to many levels with little separation, so no symmetry assignments are given in table VII. Except for the two lowest multiplets, the accuracy for Ho^{3+} is also less than for the other ions due to the large number of lines, which are often grouped very closely. The upper levels of the ground multiplet are poorly determined because of phonon interaction. No transitions to the $^5\text{I}_4$ multiplet were seen.

The lifetimes of the observed excited multiplets except $^5\text{I}_5$ are listed in table VII. The lifetimes of $^5\text{F}_4$ and $^5\text{S}_2$ are thermally coupled at room temperature. Johnson and Guggenheim⁵ have reported room-temperature lifetimes for the two lowest excited multiplets that are, within experimental accuracy,

the same as measured here. Their 5F_5 value of 70 μ s at 77 K compares to our room temperature value of 39 μ s. With a concentration lower than 1 % Ho they observe longer lifetimes. Antipenko et al.⁶ report for 0.5% doping a lifetime for 5I_7 of 9.5 ms and for 5I_6 of 4.2 ms. For 5% doping they give the lifetimes of 9.1 ms and 2.5 ms, respectively. All of these values are lower than the ones reported here.

D Erbium

All the energy levels below 25 000 cm^{-1} except one have been determined for Er^{3+} in BaY_2F_8 and are listed in table VI. Johnson and Guggenheim^{2,3} have reported the energy levels of two multiplets and a few other levels. Their crystal-field splittings of $^4F_{9/2}$ and $^4I_{15/2}$ are within the experimental accuracy equal to the splittings reported here. As for the other ions the accurate positions of the upper levels of the ground multiplet were difficult to determine. The absorption to $^4I_{9/2}$ is weak, so one level of this multiplet is missing, and the accuracy for the other levels as well as for $^4I_{11/2}$ and $^2H_{9/2}$ is less than for the other multiplets.

The lifetimes for four of the Er^{3+} multiplets are given in table VII. The values reported by Johnson and Guggenheim³ are included for comparison.

IV CONCLUSION

BaY_2F_8 is in many ways comparable to the well known laser host LiYF_4 ; the crystal can be grown the same way, and the mechanical and chemical properties are almost the same. But

there are important differences. BaY_2F_8 has lower symmetry, what makes everything a little more complicated. However, the infrared properties are better than for LiYF_4 , which makes the crystal a promising laser host in this region. It is hoped that lasing at $4\text{ }\mu\text{m}$ should be possible - maybe even at $6\text{ }\mu\text{m}$.

To get a better understanding of the crystal-field potential in this structure, the energy levels presented here together with experimental magnetic data for rare-earth doped crystals will be used to determine the crystal-field parameters. These results will be presented in some following papers. Calculated energy levels will also help to make the interpretation of the optical spectra, especially for Ho, more accurate, and permit symmetry assignments for the levels of this ion.

ACKNOWLEDGMENTS

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Table I: Refractive indices n_x , n_y , and n_z and the angle ρ between the c and z axes for BaY_2F_8 as function of the wavelength λ . Accuracy on n: 0.0001. Accuracy on ρ : 1° . Accuracy on λ : 1%.

λ (nm)	n_x	n_y	n_z	ρ ($^\circ$)
275	1.5556	1.5703	1.5457	17
300	495	631	396	19
325	435	574	339	-
350	398	530	303	20
400	338	466	244	22
450	298	421	207	23
500	270	391	179	21
600	232	353	142	21
700	208	330	120	23
800	194	314	106	21
1000	174	294	087	22
1165	160	280	074	20
1565	139	258	053	21
1965	118	239	035	20
2400	096	215	013	20
2650	1.5082	1.5201	1.5000	21

Table II: Micro hardness in Knoop numbers for BaY_2F_8 .

100 face	b :	250
	c :	275
010 face	a :	350
	c :	310
001 face	a :	350
	b :	235

Table III. Energy levels in cm^{-1} for Pr^{3+} in BaY_2F_8 at 10 K. The accuracy is $\pm 2 \text{ cm}^{-1}$ except for $^1\text{G}_4$ with $\pm 5 \text{ cm}^{-1}$. Symmetry "1" and "2" correspond to Γ_1 and Γ_2 respectively.

MULTIPLY	SYMMETRY	ENERGY	MULTIPLY	SYMMETRY	ENERGY
$^3\text{P}_2$	1	22 828 ^a	$^3\text{F}_3$	(2)	6 702
	2	721		(2)	678
	1	647		(1)	631
	1	558		(1)	550
	2	22 464		(2)	517
$^1\text{I}_6 - ^3\text{P}_1$	2	21 891 ^a		(1)	6 423
	2	776	$^3\text{F}_2$	1	5 352
	1	600		2	285
	2	472		1	273
	1	467		2	188
	2	334		1	5 167
	1	241	?	2	5 049
	2	215			
	1	21 194	$^3\text{H}_6$		4 464
$^3\text{P}_0$				2	415
	1	20 836		1	397
$^1\text{D}_2$				1	372
	1	17 042 ^a			4 314
	1	16 945 ^a	$^3\text{H}_5$		2 736 ^a
	2	745			420 ^a
	2	737			371 ^a
$^1\text{G}_4$	1	16 736			285
	2	9 971			253
	1	743			241
$^3\text{F}_4$	2	9 712		2	229
	(1)	7 247 ^a	$^3\text{H}_4$		618 ^a
	(2)	179			315
	(1)	138			268
	(2)	110		1	90
	(1)	092		1	9
	(2)	6 971		2	0
	(1)	961			
	(2)	947			
	(1)	6 936			

a) Only an approximate value

Table IV: Energy levels in cm^{-1} for Dy^{3+} in BaY_2F_8 at 10 K. The accuracy is $\pm 1 \text{ cm}^{-1}$ except for $^4\text{G}_{11/2}$, $^4\text{I}_{15/2}$, and $^4\text{F}_{9/2}$ with $\pm 5 \text{ cm}^{-1}$. All levels are doublets.

MULTIPLY	ENERGY	MULTIPLY	ENERGY	MULTIPLY	ENERGY	MULTIPLY	ENERGY
$^4\text{G}_{11/2}$	23 719	$^6\text{F}_{3/2}$	13 276	$^6\text{F}_{11/2}-^6\text{H}_{9/2}$	8 072 ^a	$^6\text{H}_{13/2}$	3 831 ^a
	579		13 269		019 ^a		674 ^a
	540		12 542		7 914 ^a		628 ^a
	518		453		854		579
$^4\text{I}_{15/2}$	479	$^6\text{F}_{5/2}$	12 423	$^6\text{H}_{11/2}$	841	$^6\text{H}_{15/2}$	555
	23 428		11 165		797		531
	22 370		129		772		3 516
	315		088		702		193
$^4\text{F}_{9/2}$	284	$^6\text{F}_{7/2}$	10 998	$^6\text{H}_{11/2}$	644		118
	246		10 428 ^a		7 604		71
	133		210		6 044		50
	074		10 167		015		8
$^6\text{F}_{1/2}$	059	$^6\text{F}_{9/2}-^6\text{H}_{7/2}$	22 018		5 950		0
	22 018		9 428 ^a		892		
	21 417		304 ^a		855		
	185		262 ^a		5 850		
	113		221				
	020		183				
	20 948		177				
	13 657		081				
			000				
			8 958				

a) only an approximate value

a) only an approximate value

Table V: Energy levels in cm^{-1} for Ho^{3+} in BaY_2F_8 at 10 K. The accuracy is $\pm 5 \text{ cm}^{-1}$ except for $^5\text{I}_7$ and $^5\text{I}_8$ with $\pm 1 \text{ cm}^{-1}$.

Multiplet	Energy	Multiplet	Energy
$^5\text{F}_3$	20 782	$^5\text{I}_6$	8 855
	779		757
	765		753
	672		746
	20 647		739
$^5\text{F}_4$	18 742		717
	717		711
	707		704
	699		700
	686		696
	650		8 687
	596	$^5\text{I}_7$	5 356
$^5\text{F}_5$	18 589		275
	18 550		271
	546		266
	532		253
	504		227
$^5\text{S}_2$	18 500		213
	15 713		196
	697		188
	685		180
	654		175
$^5\text{I}_5$	621	$^5\text{I}_8$	5 171
	579		386 ^a
	529		377 ^a
	499		349 ^a
	15 495		321 ^a
	11 310		311 ^a
	287		272 ^a
$^5\text{I}_5$	285		238 ^a
	280		119
	273		88
	262		57
	11 254		54
			39
			37
			0 ^b

a) only an approximate value

b) a quasi doublet with 0.24 cm^{-1} separation¹⁴

Table VI: Energy levels in cm^{-1} for Er^{3+} in BaY_2F_8 at 10 K.

The accuracy is $\pm 1 \text{ cm}^{-1}$ except for $^2\text{H}_{9/2}$, $^4\text{I}_{9/2}$, and $^4\text{I}_{11/2}$ with $\pm 2 \text{ cm}^{-1}$. All levels are doublets.

Multiplet	energy
$^2\text{H}_{9/2}$	24 769
	727
	672
	597
	24 531
$^4\text{F}_{7/2}$	20 723
	659
	600
	20 579
$^2\text{H}_{11/2}$	19 371
	350
	331
	233
	200
	19 168
$^4\text{S}_{3/2}$	18 518
	18 449
$^4\text{F}_{9/2}$	15 502
	423
	391
	337
	15 315

Multiplet	energy
$^4\text{I}_{9/2}$	12 687
	618
	581
	12 486
$^4\text{I}_{11/2}$	10 347
	332
	320
	307
	270
	10 226
$^4\text{I}_{13/2}$	6 780
	745
	738
	694
	606
	581
	6 530
$^4\text{I}_{15/2}$	408 ^a
	367 ^a
	324 ^a
	285 ^a
	103
	46
	25
	0

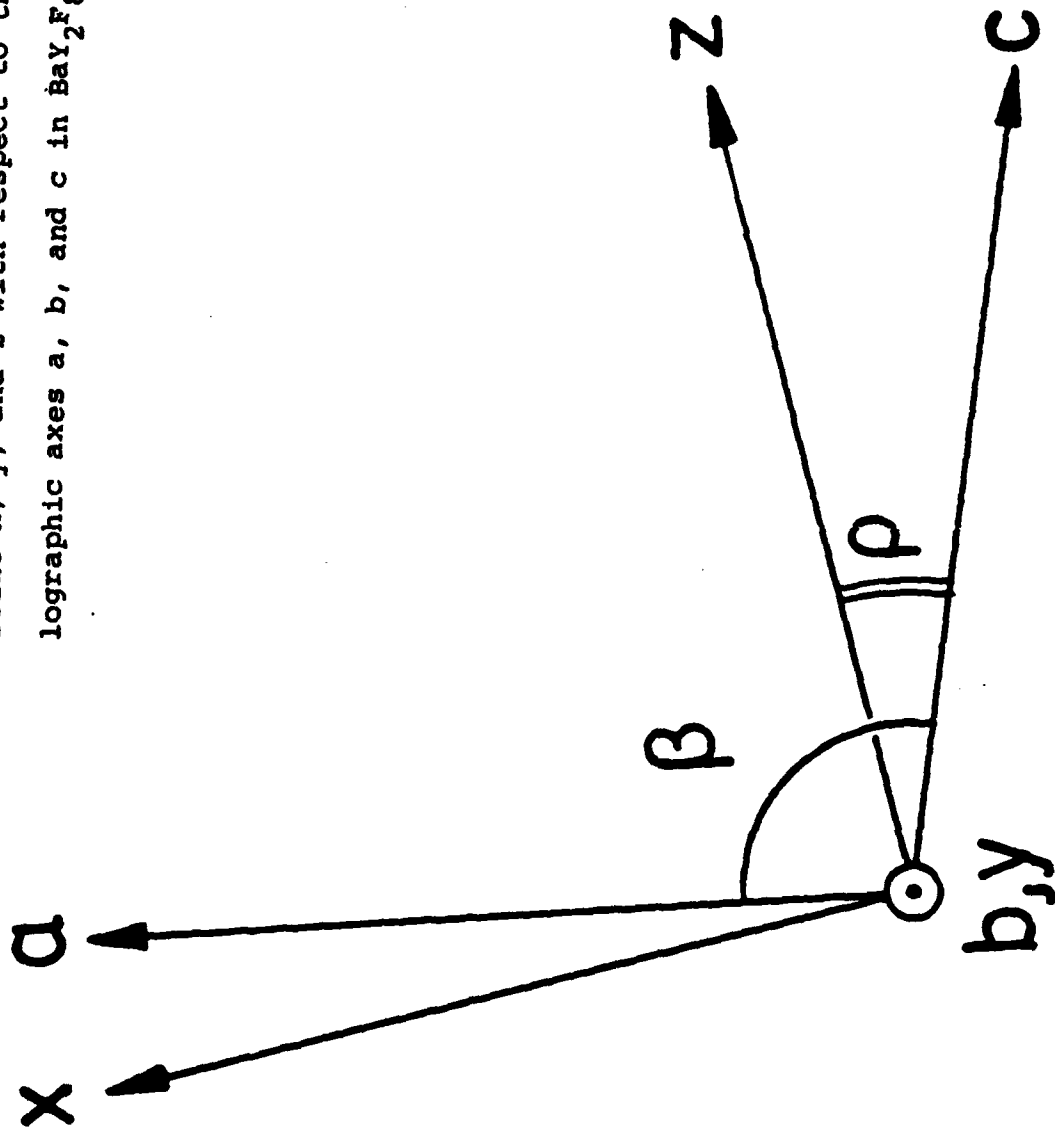
a) only an approximate value

Table VII: Fluorescent lifetimes for Pr^{3+} , Dy^{3+} , Er^{3+} and Ho^{3+} in BaY_2F_8 .

Ion and Multiplet	Concentration	Temperature	Lifetime (μs) This Work	[a]
$\text{Pr}^{3+}:^3\text{P}_0$	0.5%	300K	54 ± 3	
$\text{Dy}^{3+}:^4\text{F}_{9/2}$	1 %	300K	1280 ± 30	
$^6\text{H}_{13/2}$	1 %	300K	1500	1300^2
		77K	8000	7000^2
$\text{Ho}^{3+}:^5\text{F}_3$	1 %	300K	2.3 ± 0.1	
$^5\text{F}_4, ^5\text{S}_2$	1 %	300K	263 ± 15	
$^5\text{F}_5$	1 %	300K	39 ± 2	
		77K		70^5
$^5\text{I}_6$	1 %	300K	5400 ± 250	7000^5
	$\frac{1}{2}$ %	300K		4200^6
	5 %	300K		2500^6
$^5\text{I}_7$	1 %	300K	1700 ± 1500	16000^5
	$\frac{1}{2}$ %	300K		9500^6
	5 %			9100^6
$^4\text{S}_{3/2}$	1 %	300K	530 ± 30	
Er^{3+}		77K		830^3
$^4\text{F}_{9/2}$	1 %	300K	390 ± 30	
$^4\text{I}_{11/2}$	1 %	300K	9300 ± 700	
	20 %	77K		6700^5
$^4\text{I}_{13/2}$	1 %	300K	11700 ± 700	
	20 %	77K		8300^5

[a] Superscripts denote references.

Figure 1: The position of the axes of the index ellip-
 soide x , y , and z with respect to the crystal-
 lographic axes a , b , and c in BaY_2F_8 .



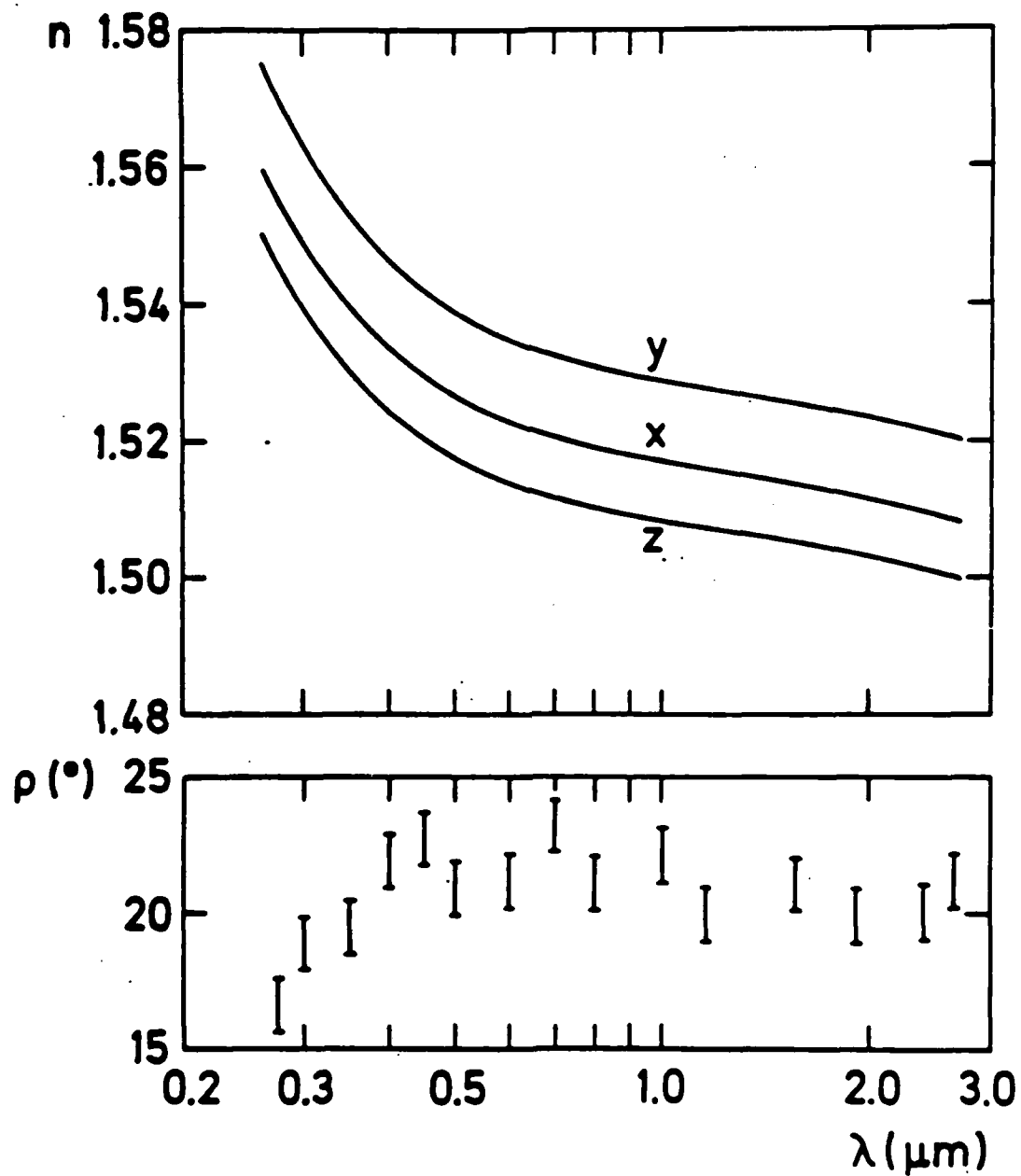


Figure 2: The refractive indices n_x , n_y , and n_z and the angle ρ between the c and z axes for BaY_2F_8 as function of the wavelength λ .

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