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Cathodoluminescence emission spectra of trivalent europium-doped yttrium oxysulphide

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Europium-doped yttrium oxysulphide phosphor ($Y_2O_2S:Eu^{3+}$) was prepared. $Y_2O_2S:Eu^{3+}$ was found to have a hexagonal structure with lattice parameters $a = 0.3776$ nm and $c = 0.6538$ nm. The cathodoluminescence emission spectra of $Y_2O_2S:Eu^{3+}$ were recorded between 400 and 635 nm at both 77 and 293 K. Most of the numerous emission lines were assigned on the basis of known energy levels of Eu^{3+} ions, crystal field splittings, and selection rules. More attention was paid to the high-intensity emission lines in the spectral red region, because this phosphor can be used as an efficient red-emitting phosphor in colour televisions. The highly intense lines at 611.3, 616.9 and 626.5 nm are attributed to the transitions from $^5D_0$ to one of the Stark components of the $^7F_2$ level. The other transitions from $^5D_1$, $^5D_2$ and $^5D_3$ to ^7F_J ($J = 0$, 1–5) were found and assigned.

1. Introduction

The chemistry and physics of rare-earth elements and their compounds have been reviewed in several articles [1–3]. The atoms of rare earths (lanthanides) differ from those of other elements, in that not only the outer electron shell but also a deeper shell is incompletely filled. For the rare-earth atoms, in the N-shell, the 4f electron is incomplete. Electron transition in this shell, caused by the absorption or emission of radiation, is little disturbed by the environment as electrons are effectively screened and shielded by the electrons in the 0 shell ($5s^2$ $5p^6$). As a result of shielding, the spectral emission lines of trivalent rare-earth ions in the host lattice are very narrow. The width of the spectral lines at room temperature is generally between 0.5 and 1 nm; the line width decreases to a small value of 0.3 nm with a decrease in the temperature to that of liquid nitrogen [4]. In this respect, compounds activated with trivalent rare earths differ considerably from most other fluorescent substances, such as II–VI or III–IV compounds, whose fluorescent spectra usually consist of broad bands [5].

Furthermore, because of the screening effect, the wavelength and width of the spectral lines are virtually independent of the nature of the matrix compound. The spectra of various phosphors activated with a particular rare-earth atom therefore show little variation in the position of the spectral lines. They are nearly similar to the spectra of a non-perturbing rare-earth ion. Owing to the crystal-field effect, however, the energy levels exhibit a more-or-less pronounced Stark splitting, so that each line is replaced by a number of neighbouring lines. Therefore the trivalent rare-earth ions were selected to be used as activators in the new class of line-emitting phosphors. The trivalent europium ion has been of particular recent interest [6, 7].

Y_2O_2S is an excellent inorganic host for incorporating the rare-earth europium ion (Eu^{3+}). The Eu^{3+} ion enters the lattice substitutionally with the need for chemical charge compensation. Also Eu^{3+} substitutes Y^{3+} without disturbing the crystal lattice where the radii of both ions are very close. Y_2O_2S has been of considerable interest in recent years [8–15]. The emission intensity of the upper ^5D levels increases by an order of magnitude, and the lower levels display a decrease of comparable size. This effect was examined by Struck and Fonger [9] who developed a model to account for the temperature dependence of the emissions of these materials.

Kaliakatosos *et al.* [16] studied the cathodoluminescence emission spectra of $Y_2O_2S:Tb^{3+}$ as a function of temperature in the range 20–300 K. The absorption and emission spectra of trivalent europium in Y_2O_3, as well as in YVO_4, were studied before by us and many other authors [17–23].

Because of the wide applications of europium-activated phosphors as red-emitting phosphors in colour television screens, this work presents the cathodoluminescence emission spectra of $Y_2O_2S:Eu^{3+}$ in the 400–635 nm range at 77 and 293 K.

2. Experimental procedure

$Y_2O_2S:Eu^{3+}$ phosphor in the form of polycrystalline powder was available for this spectral study. The phosphor was prepared by firing at 1100 °C in an oxygen-free atmosphere by Riedel–de Hean AG (Seelze, Germany).

The crystal structure of $Y_2O_2S:Eu^{3+}$ was identified by means of a Shimadzu XD-3 X-ray diffractometer. The sample was in a fine homogeneous powder. A monochromatic nickel-filtered CuK_α X-ray of wavelength 0.1542 nm was used. The diffraction pattern

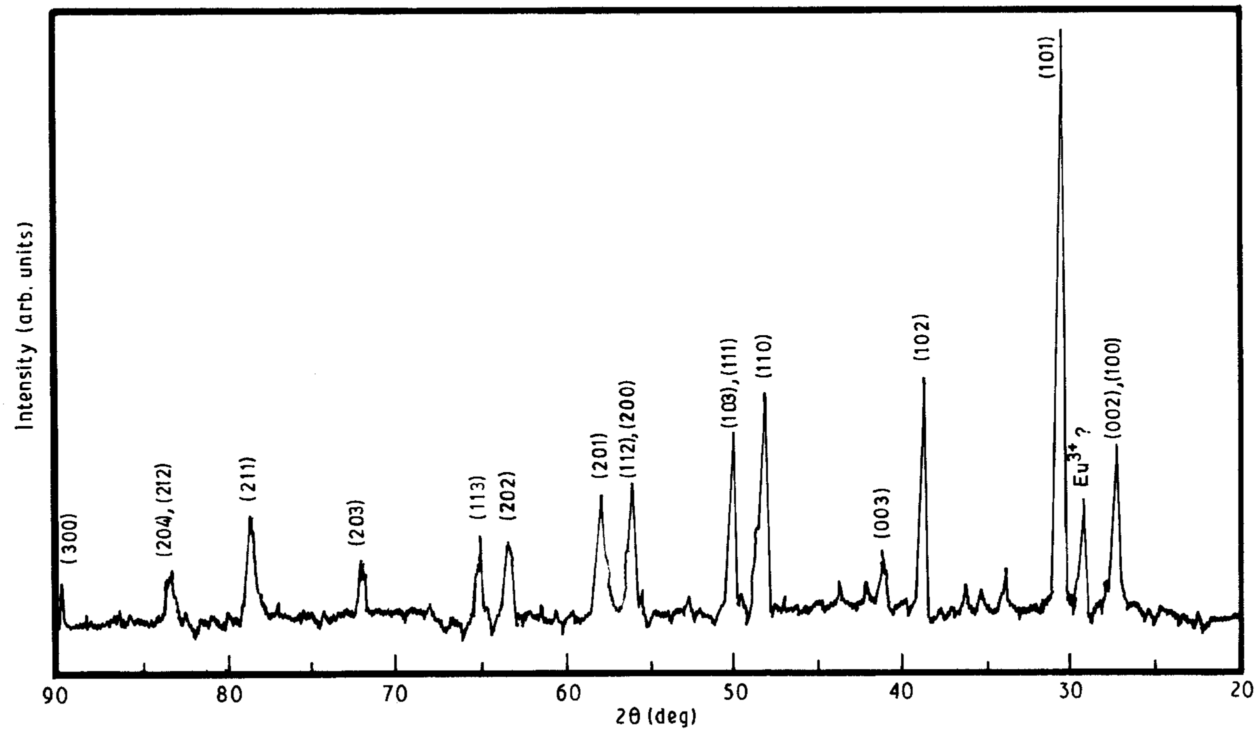


Figure 1 X-ray diffraction for $Y_2O_2S{:}Eu^{3+}$ phosphor powder at room temperature.

was recorded in terms of the intensity of the diffracted X-ray beam as a function of the diffraction angle 2θ.

For cathodoluminescence emission spectra measurements, the phosphor sample was mounted on the cold finger of the liquid nitrogen cryostat. The cryostat was evacuated to a pressure of 5×10^{-5} Pa and the sample was excited with a scanned 10-keV electron beam at a current density of 200 μA cm^{-2}. The emission of the sample was mechanically chopped at 800 Hz and analysed by a 1-m Hilger Monospek monochromator equipped with a grating of 1200 lines mm^{-1} blazed at 500 nm. Emission spectra were detected by an EMI-6255B photomultiplier tube, and recorded using a low-noise amplifier, phase-sensitive detector and potentiometric recorder. The sample temperature in the range of 77–293 K was measured by means of a copper–constantan thermocouple.

3. Results and discussion

Fig. 1 shows the XRD chart of $Y_2O_2S{:}Eu^{3+}$. X-ray analysis revealed that Y_2O_2S possesses a hexagonal crystal structure with unit cell dimensions $a = 0.3776$ nm and $c = 0.6538$ nm. These values agree with the (ASTM) index card for Y_2O_2S of $3D^3_{3d}$ ($P\,3\,\bar{m}$) space group [8, 24, 25], the point of symmetry of the yttrium site being C_{3v} (3m). The europium ion was expected to occupy the yttrium site in $Y_2O_2S{:}Eu^{3+}$, as its ionic radius of 0.112 nm is slightly larger than that of Y^{3+} (0.096 nm). Cathodoluminescence emission spectra recorded between 400 and 635 nm for $Y_2O_2S{:}Eu^{3+}$ are shown in Figs 2 and 3 at both 77 and 293 K. No emissions are detected in the spectral range 400–450 nm at 293 K. The corresponding electronic transitions involved for these emission lines are presented in Table I. The various electronic transitions

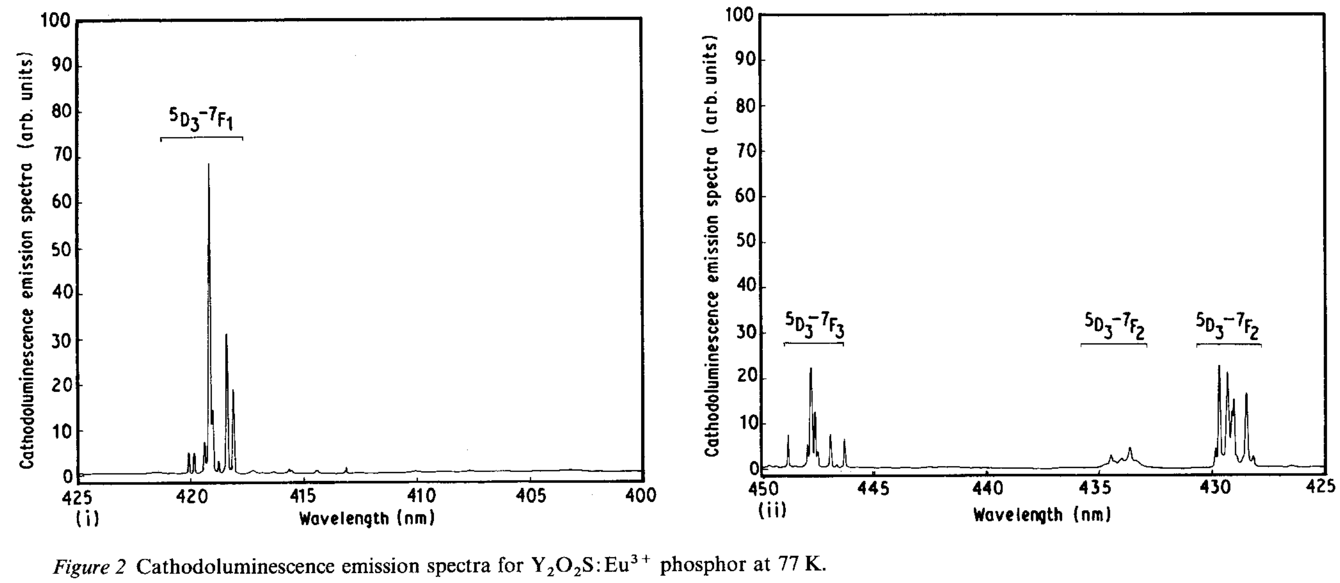


Figure 2 Cathodoluminescence emission spectra for $Y_2O_2S{:}Eu^{3+}$ phosphor at 77 K.

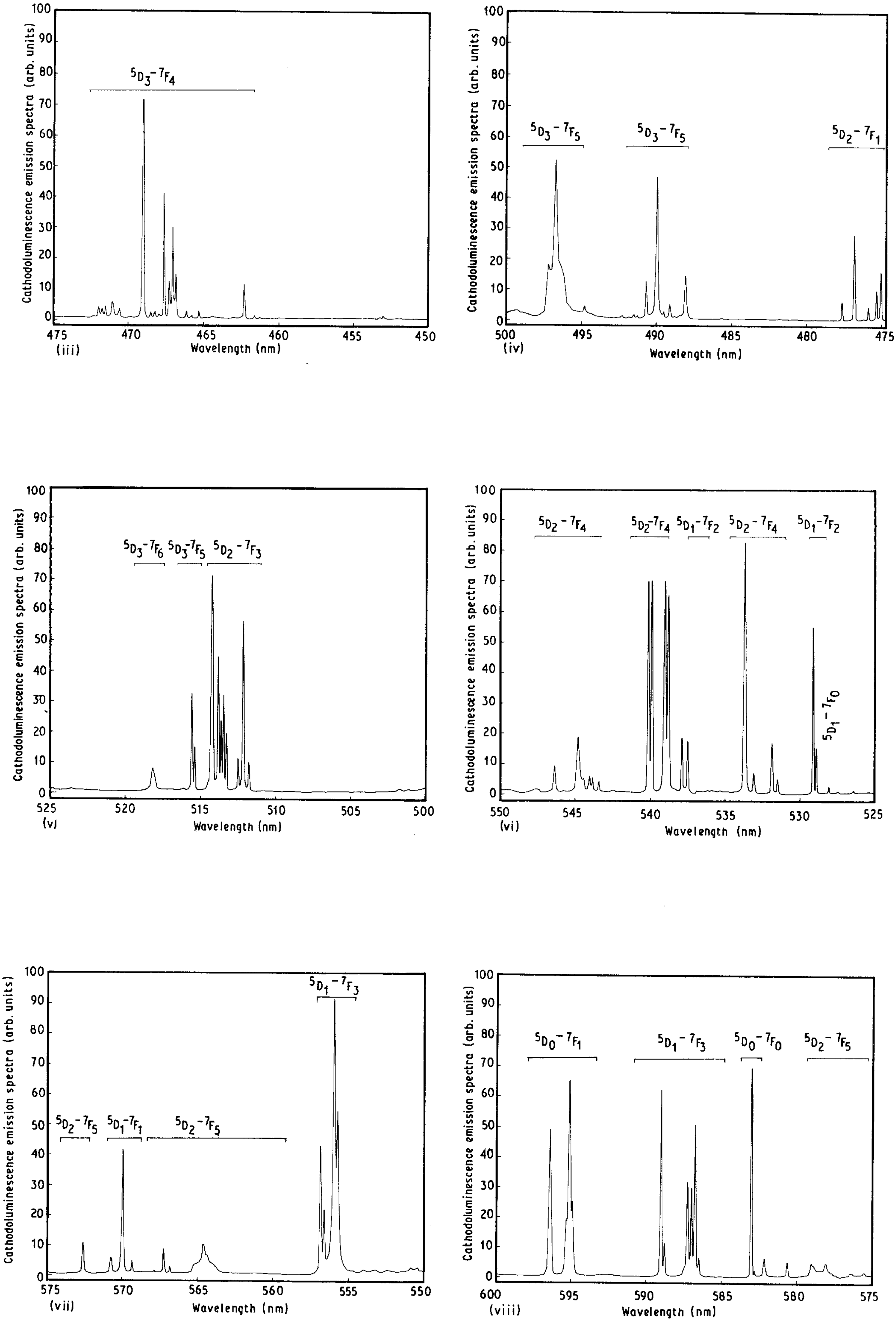


Figure 2 (Continued).

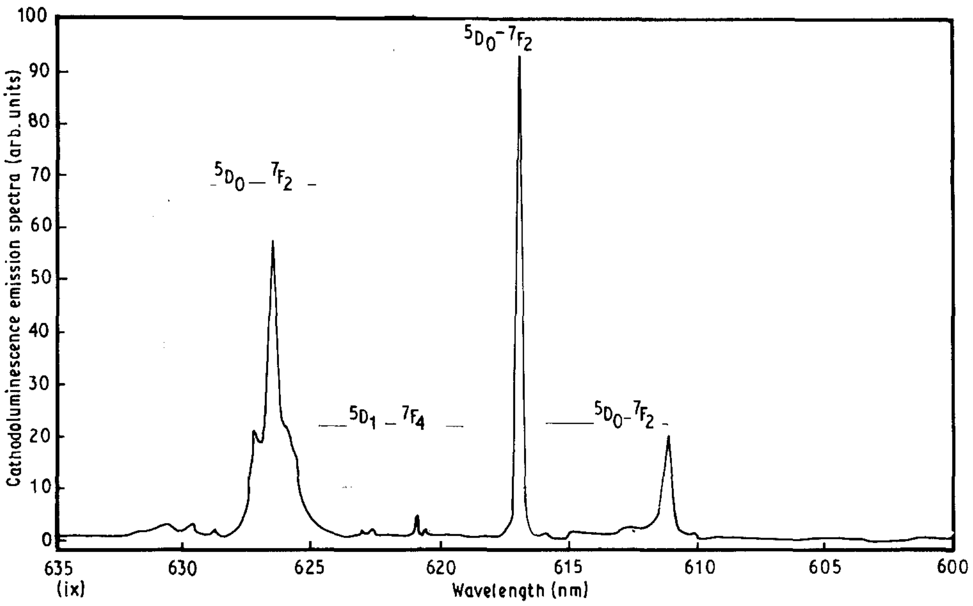


Figure 2 (Continued).

have been assigned on the basis of known energy levels of the Eu^{3+} ions and crystal field splitting in Y_2O_2S:Eu^{3+} crystals [8, 26].

As the Y_2O_2S:Eu^{3+} are used as red-light-emitting phosphors in colour televisions, we paid more attention to the emission lines in the red region. The strongest red-emission lines at 611.3, 616.9 and 626.5 nm are due to the transitions from $^5D_0$ to the $^7F_2$ levels. Other transitions from the ^5D_J ($J = 0, 1, 2, 3$) levels to other ^7F_J levels ($J = 0$ to 6) spectrum were also observed and assigned. The more intense lines were those produced by transitions from $^5D_0$ excited levels to ^7F_J levels. The effect of temperature on the location and width of the spectral lines at half maximum intensity is small. For instance, the band-width at half-maximum for the main red-emission lines 611.3, 616.9 and 626.5 nm decreases from 0.8, 0.5, and 1.6 nm at room temperature to 0.4, 0.2, and 0.5 nm, respectively, at 77 K. No spectral shifts of the emission lines have been detected with raising the temperature

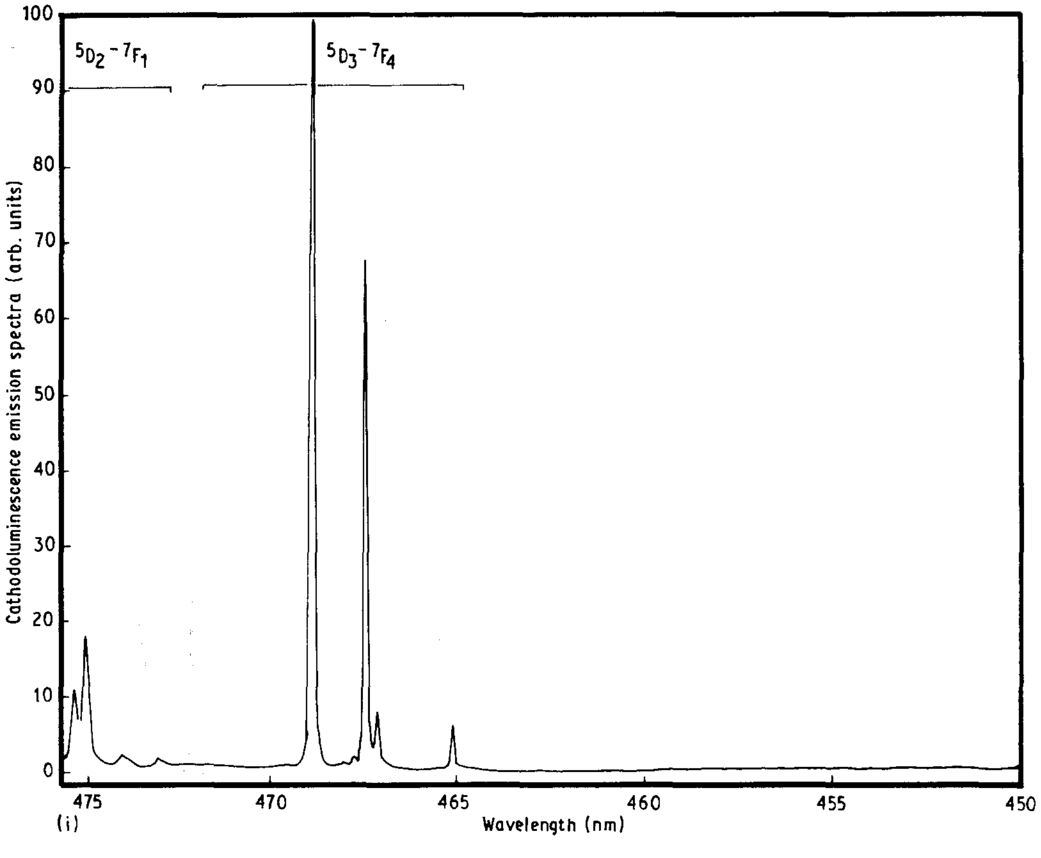


Figure 3 Cathodoluminescence emission spectra for Y_2O_2S:Eu^{3+} phosphor at 293 K.

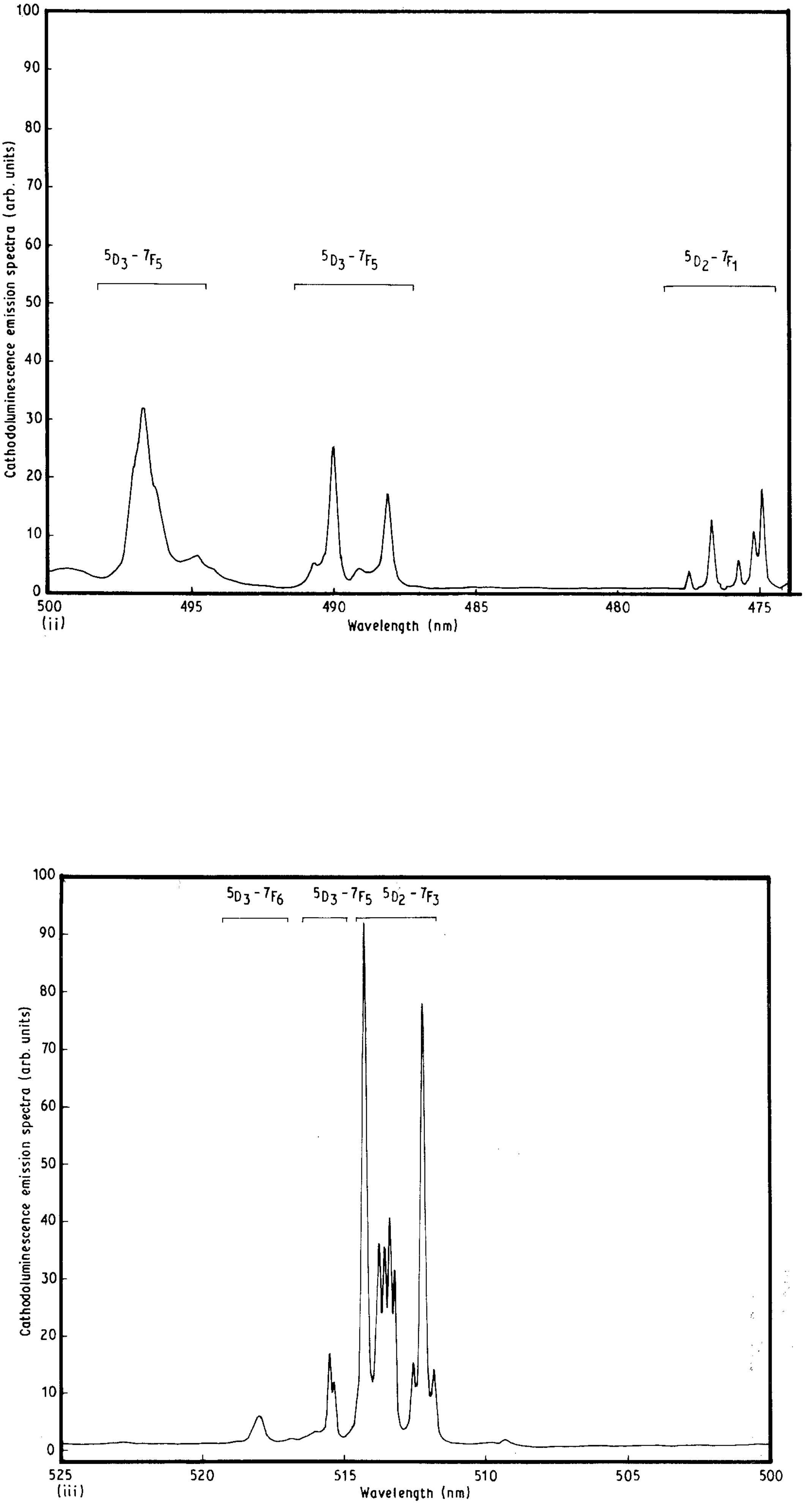
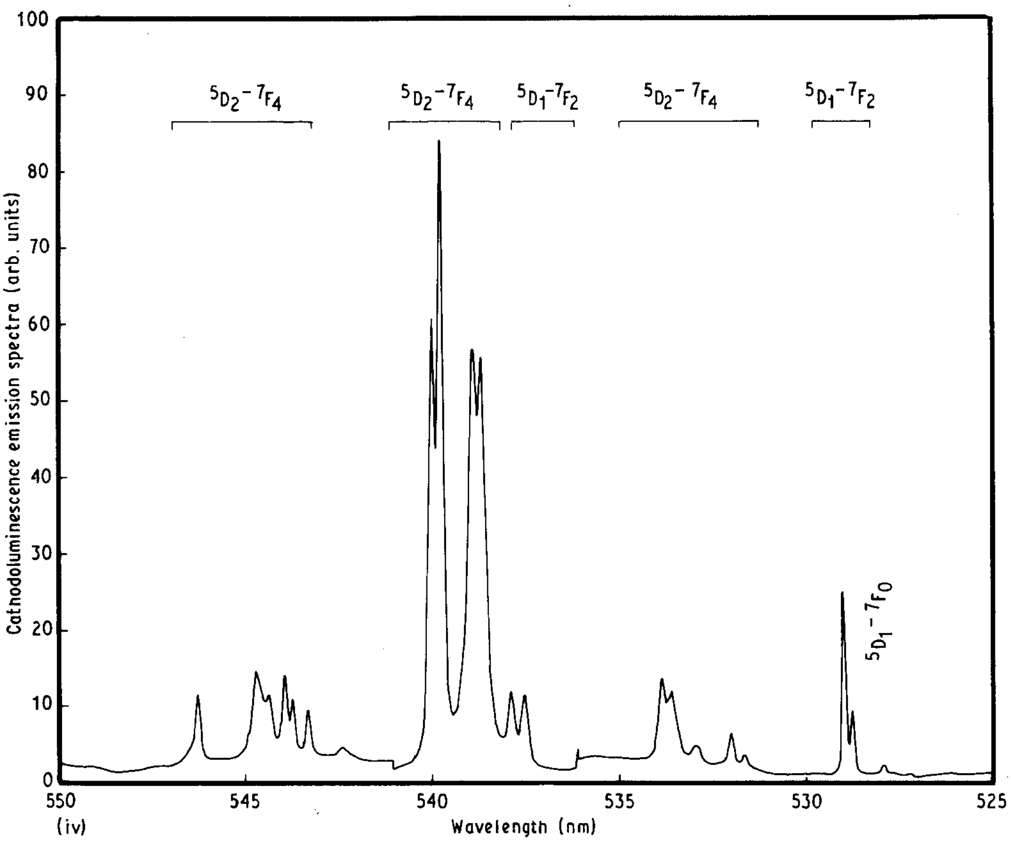


Figure 3 (Continued).



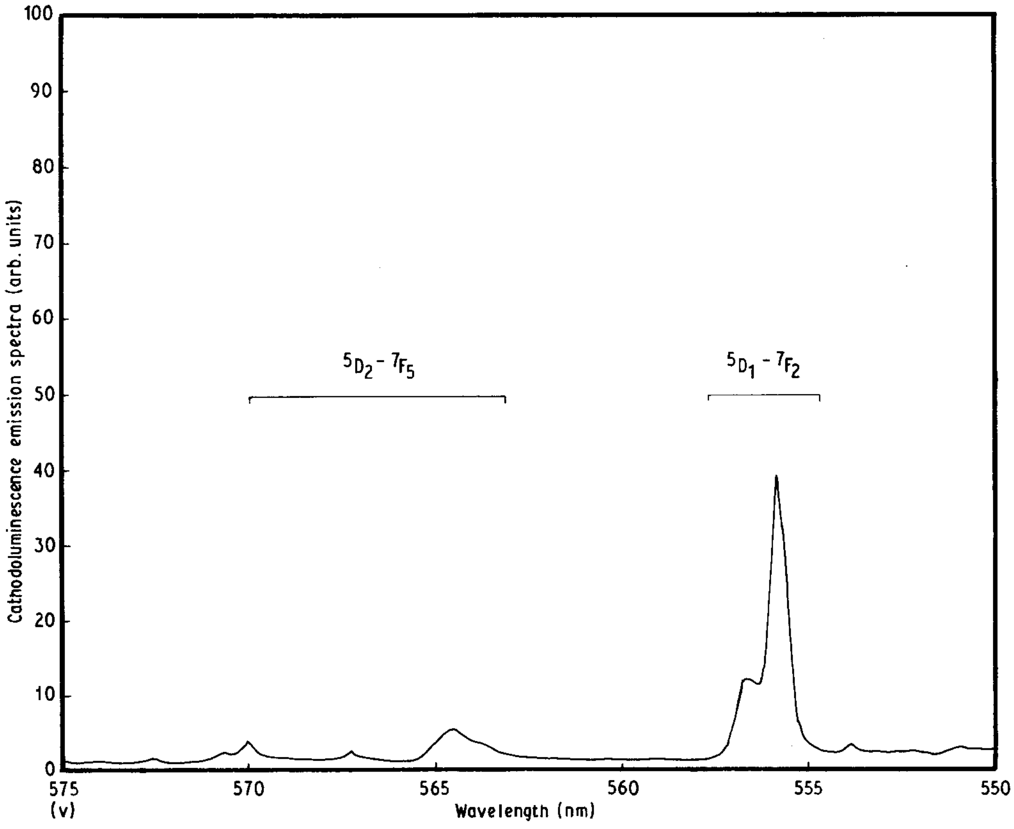


Figure 3 (Continued).

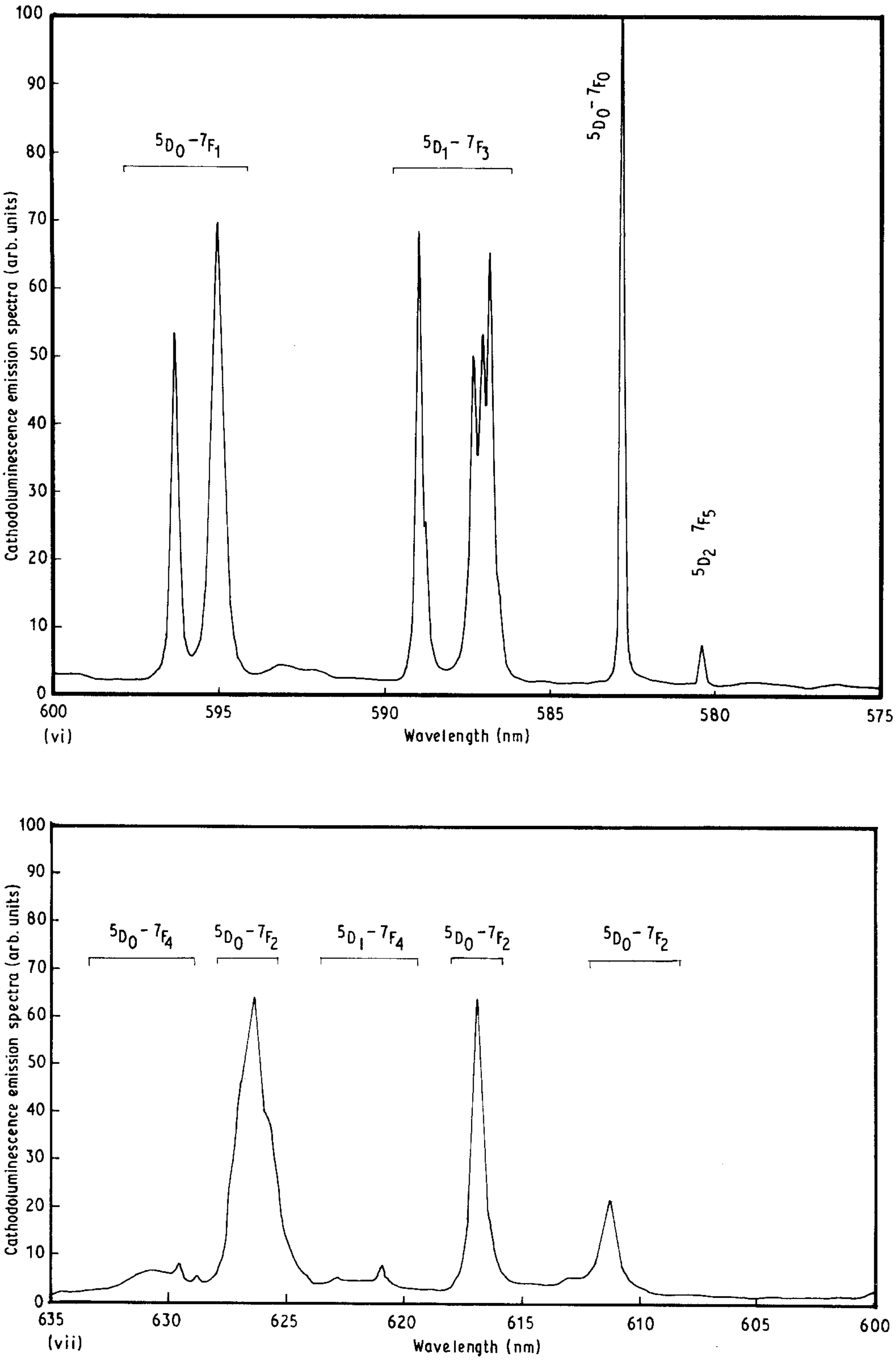


Figure 3 (Continued).

from 77 to 293 K. This is possibly due to the shielding of the electronic transitions in the $4f^6$ configuration of europium ion, by the $5s^25p^6$ electrons, from perturbation due to neighbouring atoms, i.e. shielding from crystal-field interactions. The maximum spectral shift did not exceed 0.3 nm. It is also evident that the intensities of the emission lines increased as the temperature was lowered.

4. Conclusions

Polycrystalline $Y_2O_2S:Eu^{3+}$ phosphor was found to exhibit a hexagonal crystal structure with unit cell dimensions $a = 0.3776$ nm and $c = 0.6538$ nm. The emission spectra of this phosphor consist of a large number of narrow bands. All the observed lines are assigned depending on the spectra of the free Eu^{3+} ion, spin-orbit coupling, crystal-field splitting and selection rules. It was found that the half-width of the emissions decreases as the temperature is lowered from 293 to 77 K. Due to the dramatic decrease of the intensity of the emission lines with an increase in temperature from 77 to 293 K, the emission lines due to the $^5D_3-^7F_{0,1,2,3}$ transitions cannot be detected at room temperature in the spectral region 400–450 nm.

TABLE I Cathodoluminescence emission lines of Eu^{3+} in $Y_2O_2S{:}Eu^{3+}$ at 77 and 293 K

77 K			293 K			Assignment ^5L_J
Wavelength (nm)	Wavenumber (cm^{-1})	Intensity I	Wavelength (nm)	Wavenumber (cm^{-1})	Intensity I	
413.2	24 201	0.5				$^5D_3$–$^7F_0$
418.2	23 912	5				$^5D_3$–$^7F_1$
418.5	23 894	8				$^5D_3$–$^7F_1$
418.7	23 883	0.75				$^5D_3$–$^7F_1$
419.1	23 860	4				$^5D_3$–$^7F_1$
419.2	23 855	17				$^5D_3$–$^7F_1$
419.4	23 844	2				$^5D_3$–$^7F_1$
419.8	23 821	1.25				$^5D_3$–$^7F_1$
428.3	23 348	0.75				$^5D_3$–$^7F_2$
428.5	23 337	4.25				$^5D_3$–$^7F_2$
429.1	23 304	4				$^5D_3$–$^7F_2$
429.2	23 299	3.25				$^5D_3$–$^7F_2$
429.4	23 288	5.5				$^5D_3$–$^7F_2$
429.7	23 272	5.75				$^5D_3$–$^7F_2$
429.85	23 263	1.25				$^5D_3$–$^7F_2$
433.6	23 062	1.25				$^5D_3$–$^7F_2$
434.1	23 036	0.75				$^5D_3$–$^7F_2$
434.5	23 015	0.9				$^5D_3$–$^7F_3$
446.3	22 407	1.5				$^5D_3$–$^7F_3$
446.9	22 376	2				$^5D_3$–$^7F_3$
447.5	22 346	1				$^5D_3$–$^7F_3$
447.6	22 341	3				$^5D_3$–$^7F_3$
447.8	22 331	5.5				$^5D_3$–$^7F_3$
448.8	22 282	2				$^5D_3$–$^7F_3$
462.3	21 631	3				$^5D_3$–$^7F_4$
465.3	21 491	3	465.2	21 496	1.5	$^5D_3$–$^7F_4$
465.8	21 468	1.5	467.5	21 396		$^5D_3$–$^7F_4$
468.55	21 342	2.5				$^5D_3$–$^7F_4$
469.1	21 317	72	468.8	21 328	50	$^5D_3$–$^7F_4$
470.6	21 249	3				$^5D_3$–$^7F_4$
471.2	21 222	5.5				$^5D_3$–$^7F_4$
471.55	21 206	4				$^5D_3$–$^7F_4$
471.80	21 195	3.5				$^5D_3$–$^7F_4$
472.0	21 186	4	474.8		4.5	$^5D_3$–$^7F_4$
475.2	21 043	16	475.2	21 043	2.5	$^5D_3$–$^7F_1$
475.4	21 034	10				$^5D_2$–$^7F_1$
475.8	21 017	5	475.7	21 022	1.5	$^5D_2$–$^7F_1$
476.8	20 973	28	476.7	20 977	3.25	$^5D_2$–$^7F_1$
477.7	20 934	6	477.5	20 942	1	$^5D_2$–$^7F_1$
488.15	20 486	15	488.10	20 488	4.25	$^5D_3$–$^7F_5$
489.2	20 442	5				$^5D_3$–$^7F_5$
490	20 418	48	490	20 418	6	$^5D_3$–$^7F_5$
490.7	20 379	13				$^5D_3$–$^7F_5$
491.5	20 345	2.0				$^5D_2$–$^7F_2$
492.3	20 312	1.5				$^5D_3$–$^7F_5$
494.7	20 215	5				$^5D_3$–$^7F_5$
496.7	20 132	53	496.7	20 132	8	$^5D_3$–$^7F_5$
497.25	20 110	18				$^5D_3$–$^7F_5$
511.8	19 539	10	511.8	19 539	3.5	$^5D_3$–$^7F_5$
512.2	19 524	56	512.2	19 524	19.5	$^5D_2$–$^7F_3$
512.5	19 512	11	512.5	19 512	4	$^5D_2$–$^7F_3$
513.3	19 481	19	513.2	19 485	8	$^5D_2$–$^7F_3$
513.5	19 474	32	513.4	19 478	10.25	$^5D_2$–$^7F_3$
513.65	19 469	24	513.6	19 470	9	$^5D_2$–$^7F_3$
514.85	19 460	45	513.8	19 462	9	$^5D_2$–$^7F_3$
514.3	19 444	71	514.2	19 448	23	$^5D_3$–$^7F_5$
515.45	19 401	15	515.4	19 402	3	$^5D_3$–$^7F_5$
515.60	19 395	33	515.5	19 399	4.25	$^5D_3$–$^7F_5$
518.25	19 296	8	518	19 305	1.5	$^5D_1$–$^7F_2$
528.2	18 930	0.75				$^5D_1$–$^7F_0$
528.95	18 905	4	528.7	18 914	1.25	$^5D_1$–$^7F_0$
529.2	18 894	14	529	18 904	6	$^5D_2$–$^7F_4$
531.5	18 815	1.25	531.6	18 811	1	$^5D_2$–$^7F_4$
531.9	18 801	4.25	532.0	18 797	1.5	$^5D_2$–$^7F_4$
533.15	18 756	1.75	532.9	18 765	1.25	$^5D_2$–$^7F_4$
533.70	18 737	21	533.6	18 740	3	$^5D_2$–$^7F_4$
537.5	18 605	18	537.5	18 605	5.5	$^5D_1$–$^7F_2$
537.9	18 591	19	537.9	18 591	6	$^5D_1$–$^7F_2$

TABLE I (Continued)

77 K			293 K			Assignment ${}^5L_J$
Wavelength (nm)	Wavenumber (cm^{-1})	Intensity I	Wavelength (nm)	Wavenumber (cm^{-1})	Intensity I	
538.75	18 561	65	538.7	18 563	28	${}^5D_2-{}^7F_4$
539.1	18 549	70	538.9	18 556	28.5	${}^5D_2-{}^7F_4$
539.9	18 522	70	539.8	18 525	42	${}^5D_2-{}^7F_4$
540.2	18 512	70	540	18 815	30.5	${}^5D_2-{}^7F_4$
543.4	18 403	4	543.4	18 403	2.25	${}^5D_2-{}^7F_4$
543.8	18 389	5	543.7	18 393	3	${}^5D_2-{}^7F_4$
544.1	18 379	6	544	18 382	3.5	${}^5D_2-{}^7F_4$
544.8	18 355	19	544.7	18 359	3.5	${}^5D_2-{}^7F_4$
546.4	18 305	9	546.3	18 305	3	${}^5D_1-{}^7F_2$
555.8	17 995	13.5	555.8	17 995	10	${}^5D_1-{}^7F_2$
555.95	17 987	24				
556.60	17 966	5.5				${}^5D_1-{}^7F_2$
556.80	17 960	11				
564.60	17 712	2.5	564.5	17 714	1.25	${}^5D_1-{}^7F_2$
566.80	17 643	0.75				
567.3	17 627	2				${}^5D_2-{}^7F_5$
569.4	17 562	1				${}^5D_2-{}^7F_5$
570.0	17 544	10.5	570.1	17 540	1	${}^5D_2-{}^7F_5$
570.7	17 522	1.5				${}^5D_2-{}^7F_5$
572.6	17 464	2.5				${}^5D_2-{}^7F_5$
578.1	17 298	1.25				${}^5D_2-{}^7F_5$
579.0	17 271	1.25				${}^5D_2-{}^7F_5$
580.60	17 223	1.25	580.4	17 230	2	${}^5D_2-{}^7F_5$
582.2	17 176	1.5				${}^5D_1-{}^7F_3$
583.0	17 153	69	582.8	17 158	25	${}^5D_0-{}^7F_0$
586.5	17 050	7				${}^5D_1-{}^7F_3$
586.8	17 043	51	586.8	17 041	16.5	${}^5D_1-{}^7F_3$
587.0	17 035	30	587.0	17 035	13.25	${}^5D_1-{}^7F_3$
587.3	17 027	32	587.3	17 027	12.5	${}^5D_1-{}^7F_3$
588.8	16 983	11.5				${}^5D_1-{}^7F_3$
589.0	16 976	62.5	589.0	16 978	17	${}^5D_1-{}^7F_3$
595.0	16 801	65	595.1	16 804	17.5	${}^5D_0-{}^7F_1$
596.4	16 765	49	596.3	16 770	13.5	${}^5D_0-{}^7F_1$
611.20	16 360	5	611.3	16 358	5.5	${}^5D_0-{}^7F_2$
616.95	16 209	93	616.90	16 210	16	${}^5D_0-{}^7F_2$
621.0	16 106	4.5	621	16 103	2	${}^5D_1-{}^7F_4$
622.7	16 059	2				${}^5D_1-{}^7F_4$
626.6	15 961	72	626.5	15 961	61	${}^5D_0-{}^7F_2$
627.3	15 941	21				${}^5D_0-{}^7F_2$
629.6	15 880	3				${}^5D_1-{}^7F_4$

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