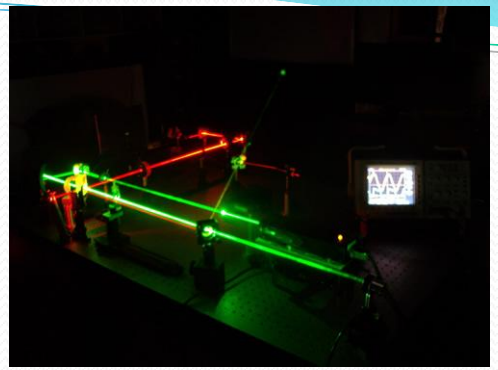

CO-DOPED SEMICONDUCTORS FOR LASER ACTIVE MEDIUM

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Outline

1. Introduction

2. Experimental procedure.

3. Results and discussions.

4. Conclusions

1. Introduction

Today, lasers and LEDs are widely used in almost all fields in medicine for diagnostics and therapeutics. Fluorescence diagnostics and Photodynamic Therapy (PDT) are typical application fields. The light source can be chosen according to the photosensitizer used. Since neither macromolecules nor water strongly absorb in the near IR, photosensitizer development has trended to activation at longer wavelengths where a “therapeutic window” delineated between 600nm and 800nm exist [3]

[1] M. J. Hammer-Wilson, C. H. Sun, M. Ghahramanlou and M. W. Berns, Lasers Surg.Med. **23,** 274 **(**1998).

1. Introduction

However, the available diode lasers operating below 630 nm which meet the PDT power requirement are expensive. In this work it is reported the growth and characterization of high quality single crystals doped with a single rare earth and a new technique of co-doped with two rare earths in order to obtain semiconductors with very high luminescence in the visible and near infrared regions. The trivalent rare earth ions are particularly useful because they produce these new lines and enhance the intensity of the emission spectra

2. Experimental procedure

The samples were prepared by chemical transport method using iodine as a transporting agent. Pure ZnSe single crystal and the other samples doped with a single rare earth and co-doped with two rare earths were grown by this method. The binary compounds were synthesized first from the high purity elements by direct flame heating in quartz ampoules under vacuum. Then, the very high quality samples were produce mixed in appropriated proportions the prepared binaries. The absorption spectra were taken, for each sample cut at the appropriate thickness, as a function of temperature between 10 K and room temperature. The experimental setup consists of a closed cycle helium cooling system, with controlled temperature, using a Cary 17 spectrophotometer.

2. Experimental procedure

The photoluminescence spectra were recorded between 550 nm and 750 nm using Labview data acquisition software as a function of temperature from 20 K to room temperature with one meter Spex monochromator. The luminescence spectra were excited by the 488 nm line of an ion-argon laser operated at 5 mW power. The optical measurements were done using an application development in the Applied Physics Laboratory on Lab View for the control and data acquisition. For the data processing and fitting, several tools on Matlab were development based on digital signal processing theory and genetic algorithms.

3. Results and discussions

Optical measurement

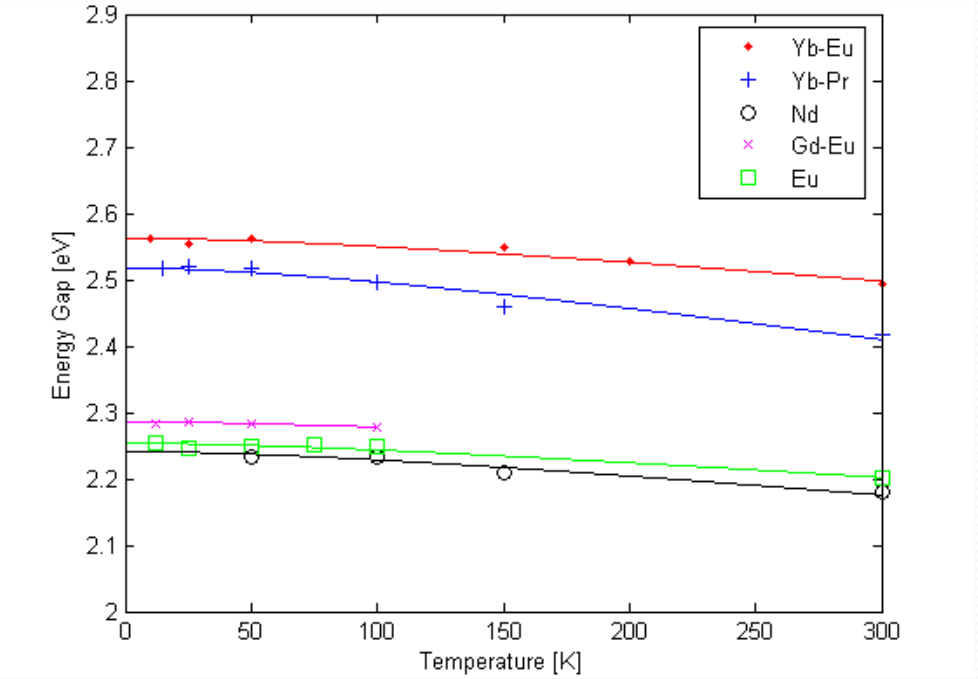

Figure 1. Energy gap variation as a function of temperature for different doping and theoretical fitting of the emission spectra observed bands as a function of temperature

3. Results and discussions

Photoluminescence measurements

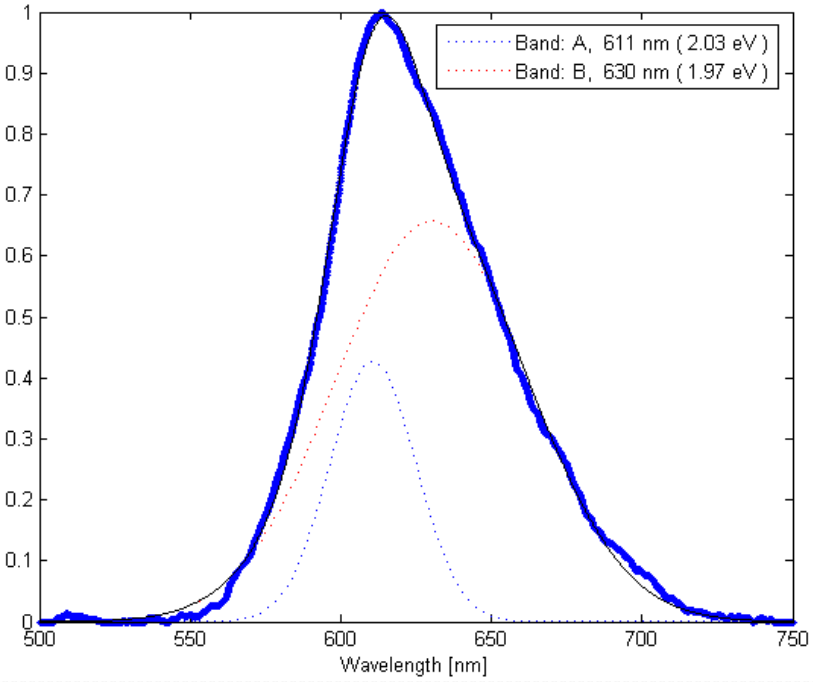

Figure 2. Photoluminescence spectra for pure ZnSe

3. Results and discussions

Photoluminescence measurements

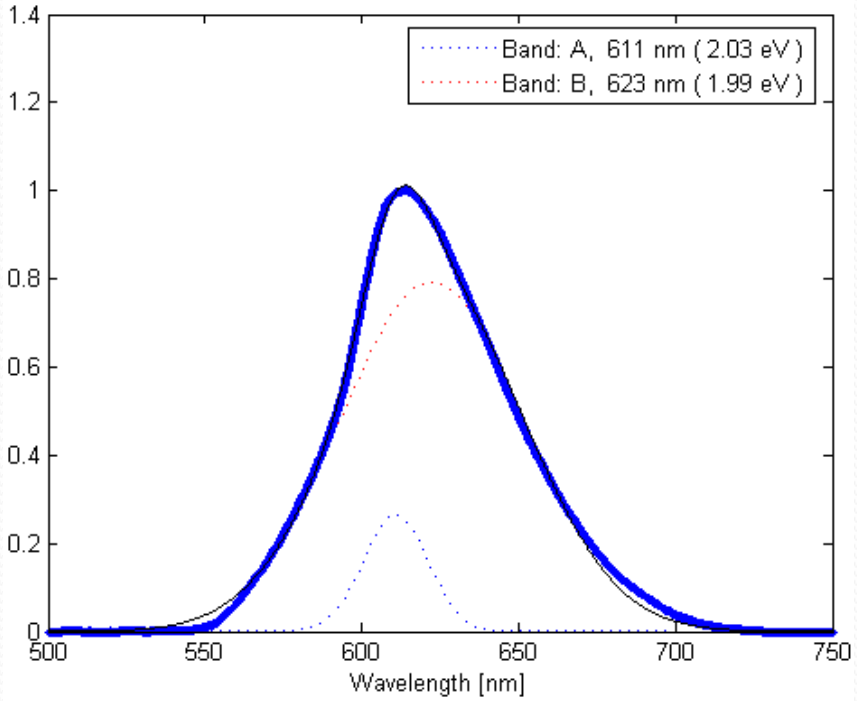

Figure 3. Photoluminescence bands of ZnSe doped with Europium.

3. Results and discussions

Photoluminescence measurements

The emission spectrum is basically the same as pure ZnSe, but more intense. A surprising result is obtained when this semiconductor is co-doped with the two rare earths Yb and Eu, the spectrum is richer in new narrow emissions and very intense lines appear in the spectrum, these lines do not shift with temperature.

3. Results and discussions

Photoluminescence measurements

Temperatura						Asignación
20K	50K	75K	100K	150K		
λ(nm)					ν(cm⁻¹)	
743,9					13.443	$^5D_0 \rightarrow {}^7F_5$ *
739,6					13.521	*
733,9					13.626	*
720,6	720,7	720,9	720,9	720,9	13.872	*
711,7	710,4	711,4	711,5	711,2	14.061	
707,3	708,8	709,3	709,2	708,9	14.106	$^5D_1 \rightarrow {}^7F_6$
	705,1	705,7	705,7	705,7	14.170	$^5D_1 \rightarrow {}^7F_6$
700,0	699,9	699,9	700,5	700,0	14.286	
695,7		696,4	696,2	695,9	14.370	**
689,7	689,6	690,0	689,9	689,8	14.496	$^5D_0 \rightarrow {}^7F_4$ **
672,3		678,1	680,2	680,0	14.706	**
666,9		668,5	668,5	668,7	14.957	
660,4	661,9	661,8	661,8	661,7	15.113	$^5D_0 \rightarrow {}^7F_3$
657,6	657,5	657,6	657,6	657,7	15.205	$^5D_1 \rightarrow {}^7F_5$
610,3	610,3	610,4	610,0	610,2	16.388	$^5D_0 \rightarrow {}^7F_2$
604,8	604,7	604,3	604,8	604,7	16.537	$^5D_0 \rightarrow {}^7F_1$
	595,9	599,2			16.781	$^5D_2 \rightarrow {}^7F_6$
	544,4	544,0			18.368	
	534,5	534,6			18.705	$^5D_1 \rightarrow {}^7F_1$

* and ** Degeneration of the transition in cubic crystal field

Table 1. Photoluminiscence measurements in ZnSe: Eu - Yb

3. Results and discussions

Photoluminescence measurements

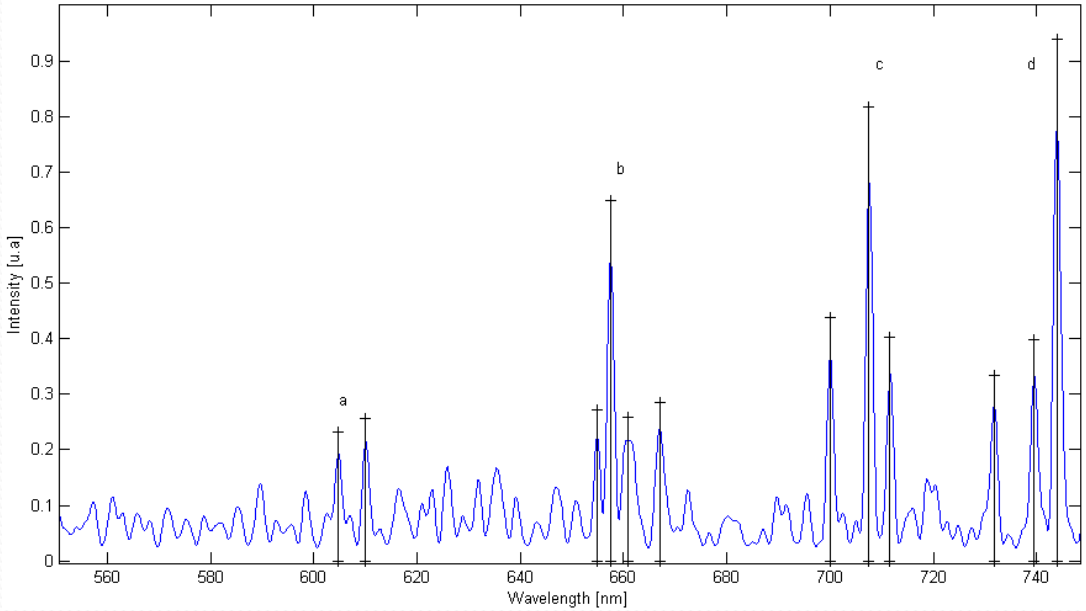

Figure 4. Photoluminescence spectra of ZnSe doped with Yb and Eu at 20K.

3. Results and discussions

Photoluminescence measurements

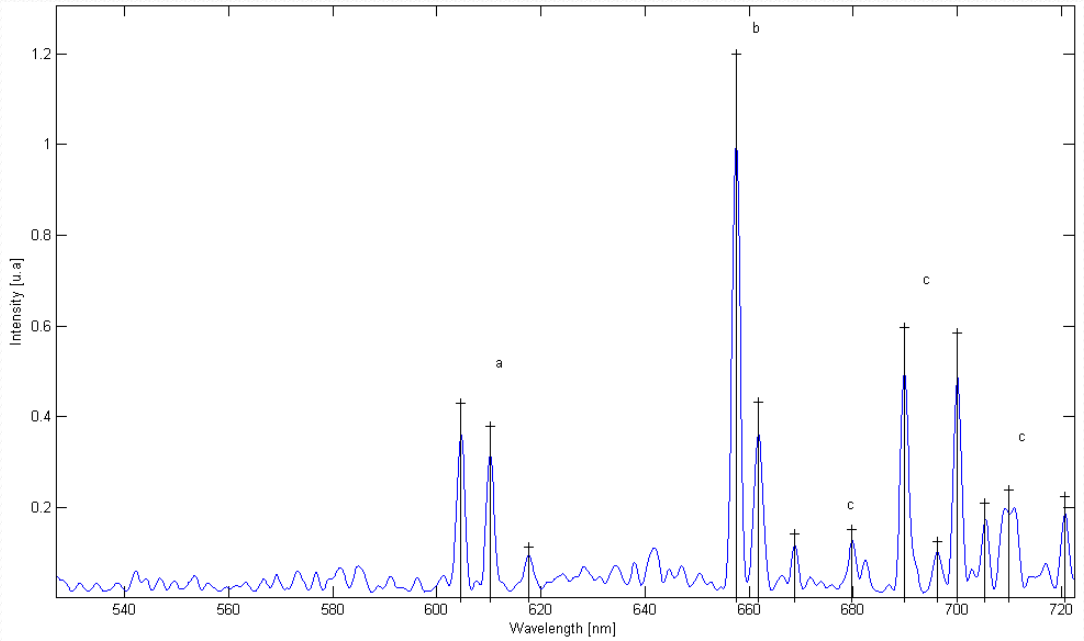

Figure 5. Photoluminescence spectra of ZnSe doped with Yb and Eu at 200K

3. Results and discussions

Photoluminescence measurements

Temperatura (K)						Asignación
18	50	75	100	150		Preliminar
λ(nm)					ν(cm⁻¹)	
744,3	744,3	744,3	744,3	744,3	13435	$^3P_0 \rightarrow {}^3F_4$ *
739,3	739,3	739,3	739,1	739,4	13524	*
731,8	731,9	732,0	732,1	731,8	13665	*
709,5	709,4			709,7	14090	**
700,0	700,2	700,2	700,2	700,2	14282	$^3P_0 \rightarrow {}^3F_3$ **
690,3	690,6	690,4	690,6	690,5	14482	**
670,2	670,0	670,0	689,4	689,4	14921	
661,8	661,9	661,9	661,8	661,8	15110	$^1D_2 \rightarrow {}^3H_5$
657,6	657,6	657,7	657,8	657,5	15207	$^3P_0 \rightarrow {}^3F_2$
	617,3	617,3	617,3	617,3	16200	$^3P_0 \rightarrow {}^3H_6$
610,2	610,1	610,0	610,1	610,2	16388	$^1D_2 \rightarrow {}^3H_4$
		604,4	605,2	604,8	16534	
	566,2	566,1	566,2	566,2	17661	
	562,9	563,0	562,9	563,0	17761	
	556,6	556,5	556,7	556,8	17966	
	544,5	544,3	544,4	544,3	18369	$^3P_0 \rightarrow {}^3H_5$ *
532,9	532,6	532,5	532,6	532,6	18776	*
	531,4	531,5	531,5	531,4	18815	*

* and ** Degeneration of the transition in cubic crystal field

Table 2. Photoluminiscence structures for ZnSe: Pr

3. Results and discussions

Photoluminescence measurements

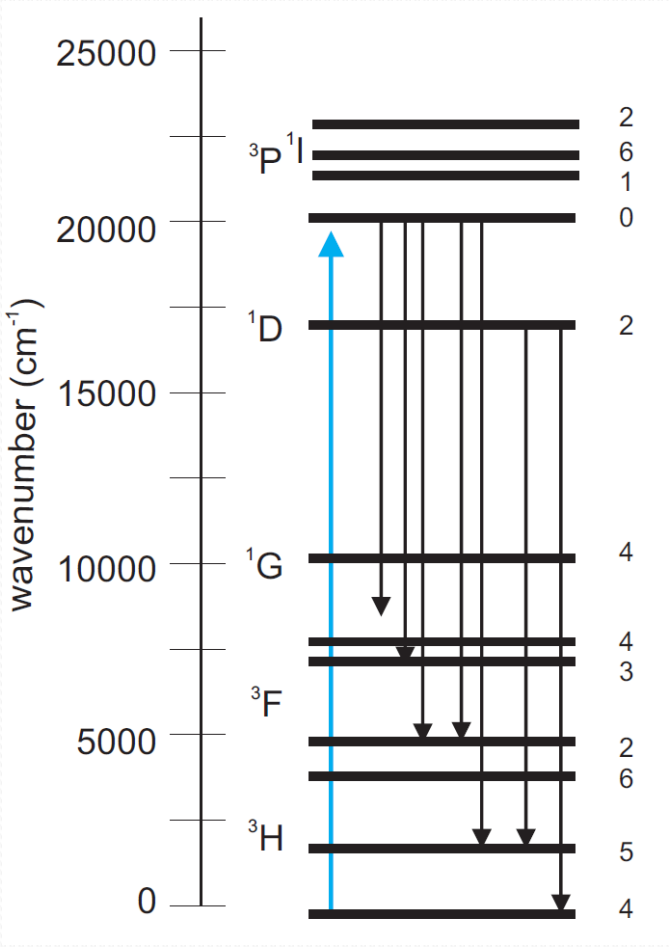

Figure 6. Absorption and emission spectra of ZnSe doped with Pr at 200K

3. Results and discussions

Photoluminescence measurements

18K	25K	50K	75K	100K	150K	200K	250K	
λ(nm)								Banda
619,0	616,0	604,8	615,5	615,3	615,7	634,7	634,5	B
646,8	644,4	636,1	647,9	647,4	647,5	666,0	666,0	A

Table 3. Photoluminiscence structures for ZnSe: Er

3. Results and discussions

Photoluminescence measurements

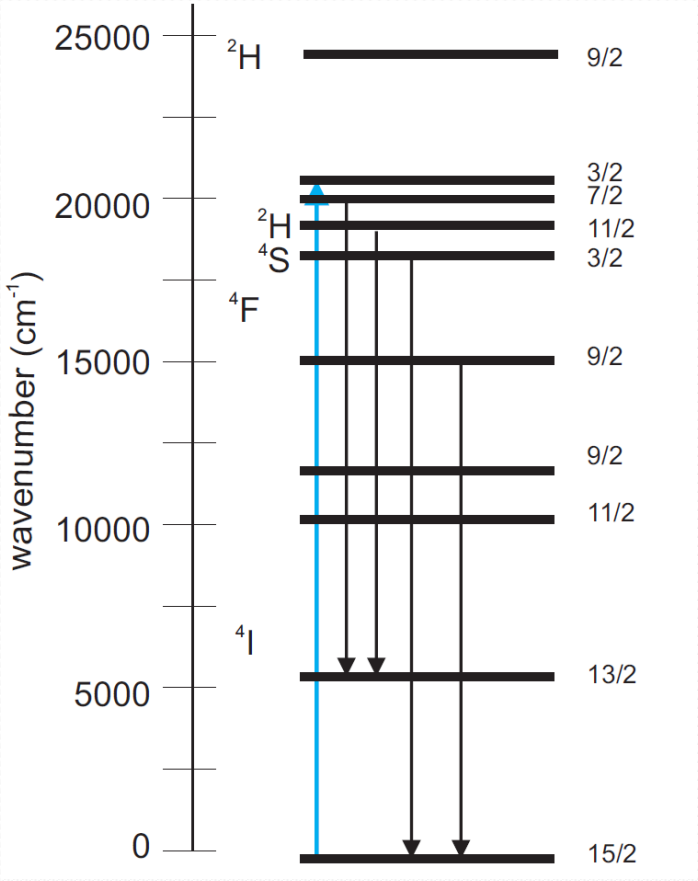

Figure 7. Absorption and emission spectra of ZnSe doped with Er at 200K

4. Conclusions

1. We have proven that it is possible to prepare doped II-VI semiconductor with one and two rare earths simultaneously.
2. The emission spectra of these materials give new narrow and very intense lines in the visible and near infrared regions important for future diode lasers and LEDs developments with adequate power at relevant wavelengths .
3. The correlation between the theory and the experimental results is in good agreement within the experimental error.
4. In addition, these materials have emission spectra within the “therapeutic window” of human body which could have very important clinical utility.

Thanks for your attention

Anexos

The trivalent rare earth ions are particularly useful because they produce these new lines and enhance the intensity of the emission spectra, for the following reasons:

The f-electron absorption transitions are much weaker than those of the *d* electrons. This permits used much higher active ion concentrations without complications from extensive self-absorption or excitation depletion.

The total emission spectra for a single metastable state of the trivalent rare earth ions change little with concentration. This allows estimating the changes in total emission by monitoring a reasonably narrow band of frequencies.

The overall quantum efficiencies of emission for excitation absorbed directly by the single rare earth ions are of the order of unity in many instances.

The two rare earth co-doping gives the possibility of optical pumping between the f electron quantum levels of one rare earth to the other.

Anexos

Se calculó la brecha de absorción directa utilizando la relación:

$$\alpha = \frac{A}{h\upsilon}\left(h\upsilon - E_g\right)^{1/2}$$

La brecha de energía fue encontrada por la intercepción analítica para una absorción cero, de la gráfica lineal $(\alpha h\nu)^2$ contra $h\nu$.

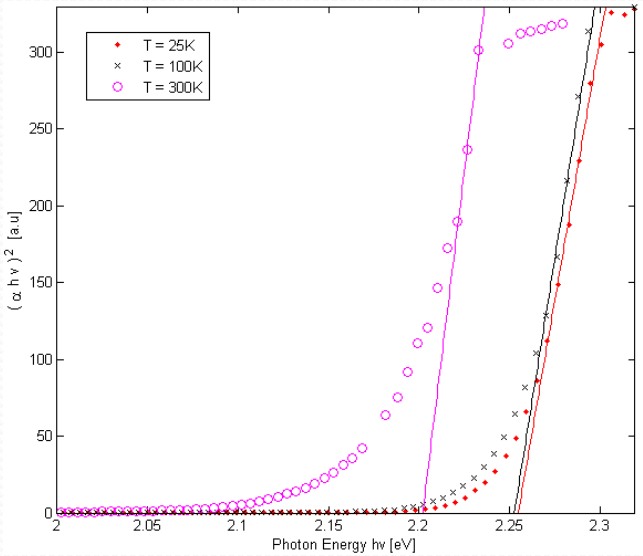

Figure 1. Energy gap calculation plot

Temp.(K)	Eu	Nd	Gd-Er	Nd-Yb	Pr-Yb	Eu-Yb
15	2,225		2,283	2,252	2,518	2,562
25	2,216	2,204	2,286	2,252	2,521	2,554
50	2,228	2,234	2,283	2,248	2,516	2,562
75	2,250			2,243		
100	2,249	2,234	2,277	2,253	2,496	
150		2,199		2,221	2,446	2,548
300	2,201	2,204		2,186	2,415	2,492

Tabla1. Valores de la Brecha de energía directa en eV, para cada temperatura

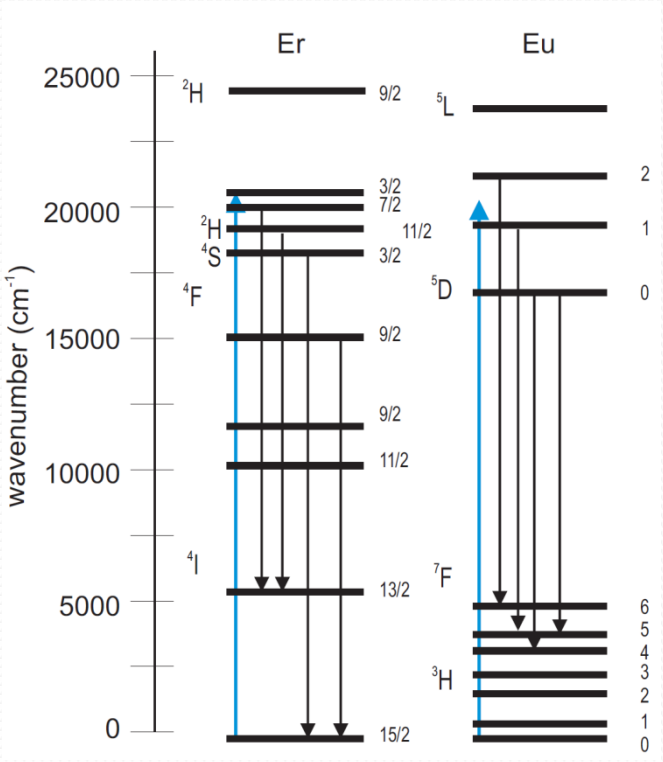

Figure 2. Absorption and emission spectra of ZnSe doped with Er and Eu at 200K