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INFRARED SENSORS USING ENERGY  
TRANSFER/ENERGY UPCONVERSION  
PROCESSES: STUDY OF LASER EXCITED  
FLUORESCENCE IN RARE EARTH ION  
DOPED CRYSTALS Final Report (NASA)  
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## DEVELOPMENT OF INFRARED SENSORS USING ENERGY TRANSFER/ENERGY UPCONVERSION PROCESSES: STUDY OF LASER EXCITED FLUORESCENCE IN RARE EARTH ION DOPED CRYSTALS

(MSFC Center Director's Discretionary Fund Final Report,  
Project No. 91-10)

By S.K. Nash-Stevenson, B.R. Reddy, and P. Venkateswarlu

Astrionics Laboratory  
Science and Engineering Directorate

February 1994



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Space Administration

George C. Marshall Space Flight Center



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<b>14. SUBJECT TERMS</b>  LaF <sub>3</sub> :Ho <sup>3+</sup> , LaF <sub>3</sub> :Er <sup>3+</sup> and CaF <sub>2</sub> :Nd <sup>3+</sup> , upconverted emissions			<b>15. NUMBER OF PAGES</b> 19	
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## DEFINITION OF SYMBOLS

### Symbol

### Definition

$\text{LaF}_3:\text{Ho}^{3+}$	Lanthanum fluoride with triply ionized holmium
$\text{LaF}_3:\text{Er}^{3+}$	Lanthanum fluoride with triply ionized erbium
$\text{CaF}_2:\text{Nd}^{3+}$	Calcium fluoride with triply ionized neodymium





## TECHNICAL MEMORANDUM

### DEVELOPMENT OF INFRARED SENSORS USING ENERGY TRANSFER/ENERGY UPCONVERSION PROCESSES: STUDY OF LASER EXCITED FLUORESCENCE IN RARE EARTH ION DOPED CRYSTALS

(MSFC Center Director's Discretionary Fund Final Report, Project No. 91-10)

#### INTRODUCTION

Rare Earth ion doped materials have been investigated extensively and have proven to be very useful in the generation of laser sources, luminescent materials, detection of infrared radiation, and in the production of upconversion lasers. Specifically, these materials can convert infrared energy into visible energy or long wavelengths into short wavelengths. Sequential two-photon/multiphoton excitation, energy transfer interaction, and excited state absorption were found to be the mechanisms responsible for the production of the energy upconverted emissions in rare earth ion doped crystals. Utilizing one or more of these mechanisms, ions in a lower energy state get upconverted to a higher energy state whose energy is greater than that of the incoming photon, and subsequently emit high energy photons.

Development of infrared sensors using energy upconversion processes could eliminate the cooling required for some infrared sensors. However, the process and specific material would have to be identified. Under CDDF Project No. 91-10, laser spectroscopic studies of different rare earth ion doped  $\text{CaF}_2$  and  $\text{LaF}_3$  crystals were carried out at room temperature for this purpose. Three systems were identified which generated upconversion radiation and a discussion of the results is presented.

#### $\text{LaF}_3:\text{Ho}^{3+}$

A partial energy level diagram of  $\text{Ho}^{3+}$  is shown in figure 1. The dye laser excited fluorescence is identified with solid lines, and the infrared laser excited fluorescence is identified with dashed lines. When the crystal was exposed to 800-nm laser radiation, a bright green emission from the material was detected and visible to the naked eye. The resulting fluorescence was analyzed and found to arise from the E, F, and D levels as identified in figure 2. The 800-nm laser excites only the phonon coupled levels of the B state. However, the laser is in exact resonance from the excited state A to the higher G state. A plot of F→Z fluorescence versus laser power exhibited a gradient of 1.5 (fig. 3). This indicates that more than one photon is responsible for the production of green emission. It was determined that the excited ion relaxes to the A state and is then excited to the G state by another laser photon. In this case, the 800-nm photon is resonant with the A→G transition. The G state relaxes to the F and E states in cascade which emit the blue, 485-nm (F→Z), and green, 546-nm (E→Z), radiation.

When the D levels of  $\text{Ho}^{3+}$  were resonantly excited with a 640-nm dye laser beam, upconverted emissions were detected from the E, F, and J levels at 546 nm (E→Z), 485 nm (F→Z), and 416 nm (J→Z), respectively (fig. 4). The sample exhibited bright green fluorescence visible to the naked eye even for 30 mW of input laser power. A plot of upconverted blue signal intensity (F→Z) versus laser power exhibited a gradient of 1.75 when the laser beam was focused in the sample and a value of 2.0

when it was defocused (fig. 5). This is a clear indication that excited state population is getting saturated. The 640-nm laser photon is resonant with Z→D and A→J transitions, and such a sequential two-photon excitation process is responsible for the production of the upconverted emission. The lower F and E levels were populated in cascade by multiphonon emission from the J state and emit blue and green light. The estimated energy upconversion efficiency was found to be  $\sim 1.1 \times 10^{-4}$ .

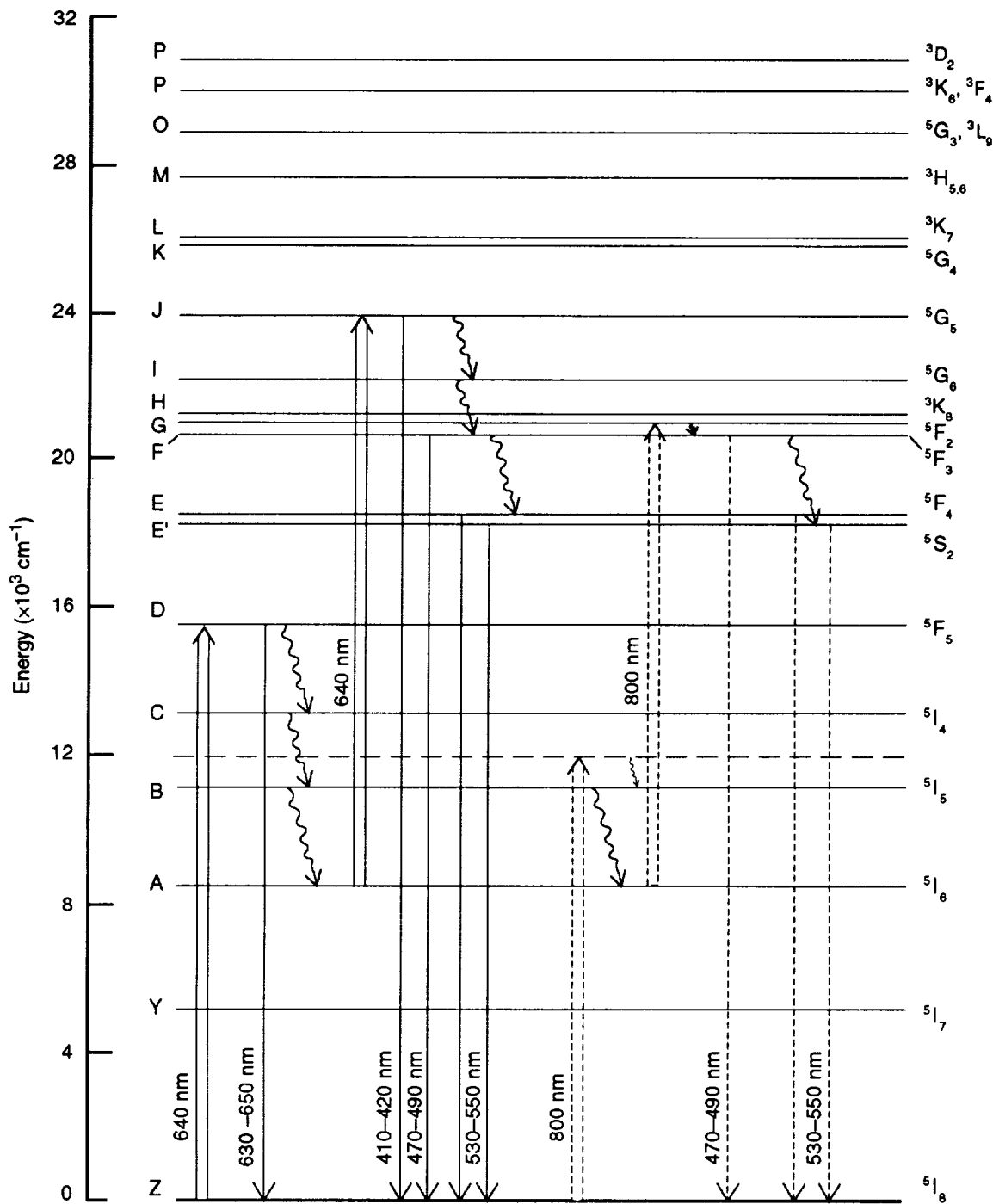


Figure 1. Partial energy level diagram of  $\text{LaF}_3:\text{Ho}^{3+}$  showing observed fluorescence transitions.

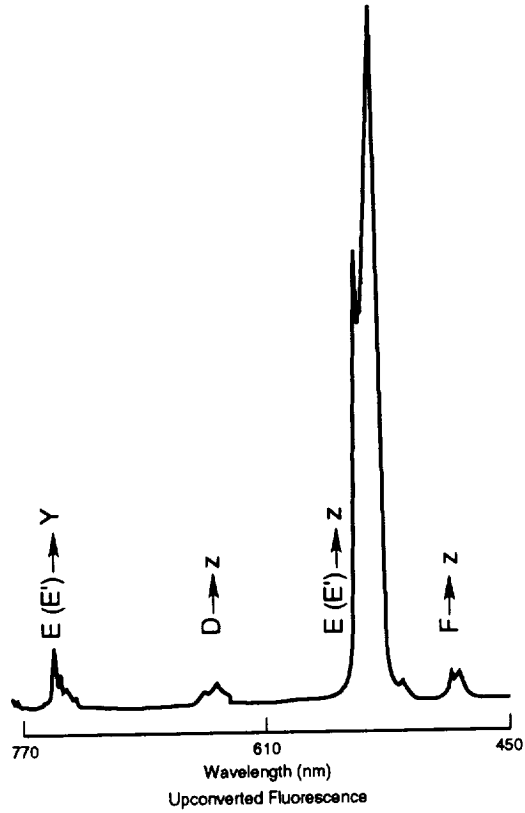


Figure 2. Upconverted fluorescence spectrum of  $\text{LaF}_3:\text{Ho}^{3+}$  obtained by pumping the material with a near infrared laser (800 nm).

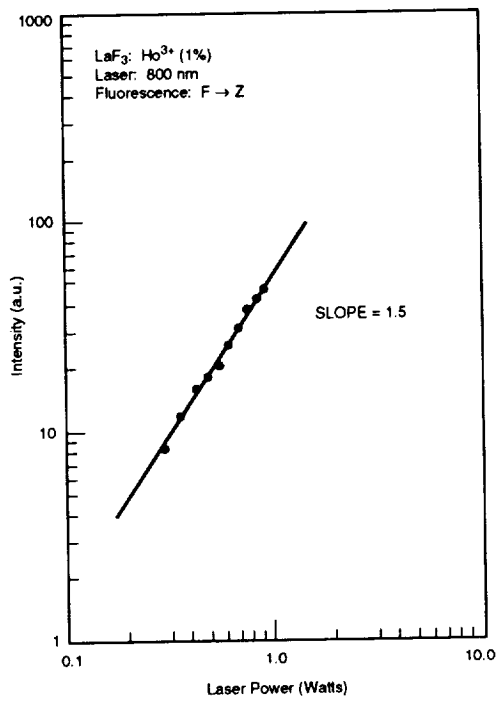


Figure 3. Power versus intensity plot of the F→Z band of  $\text{LaF}_3:\text{Ho}^{3+}$  using 800-nm laser excitation.

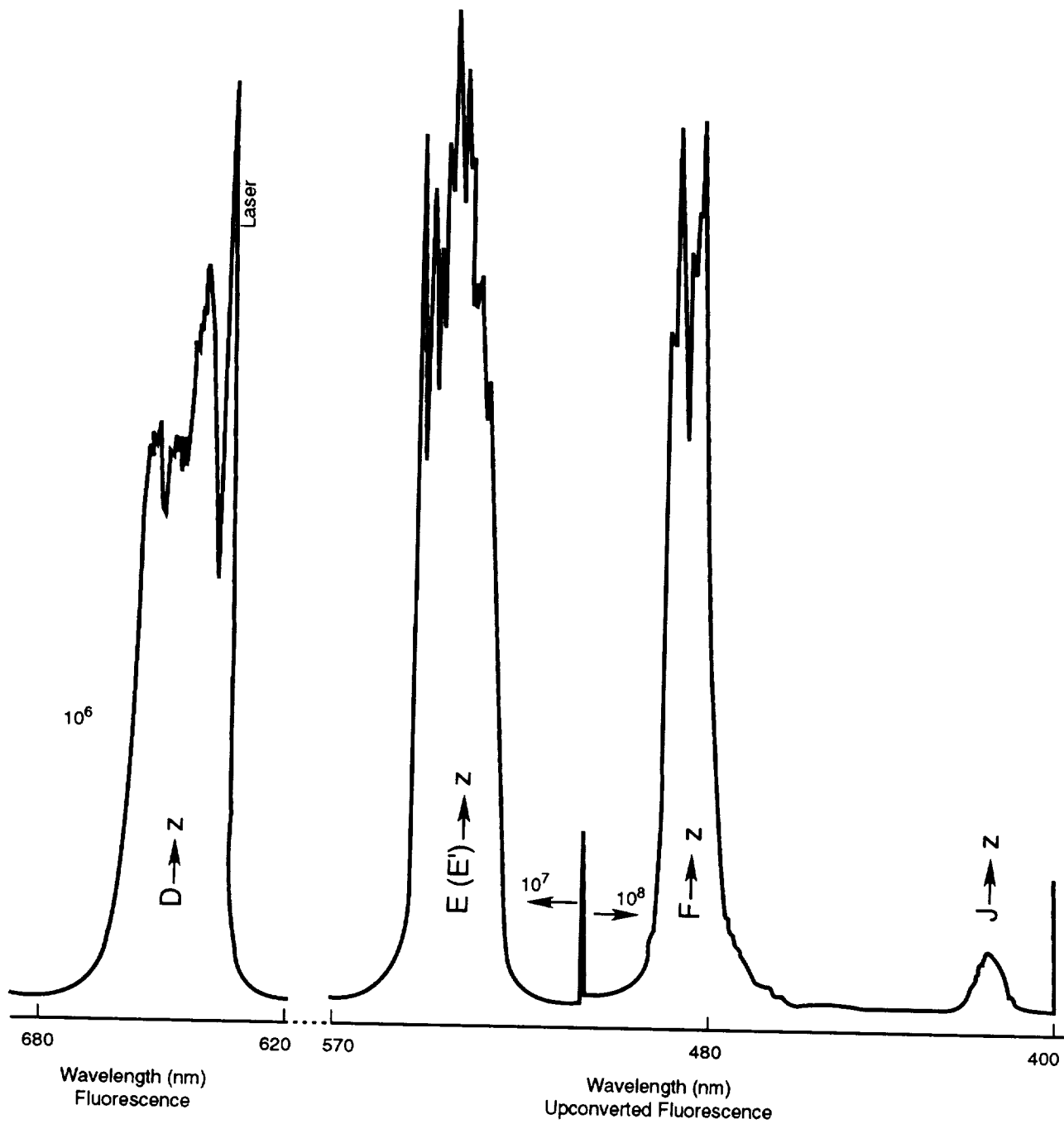


Figure 4. Fluorescence spectrum of  $\text{LaF}_3:\text{Ho}^{3+}$  using 640-nm laser excitation.

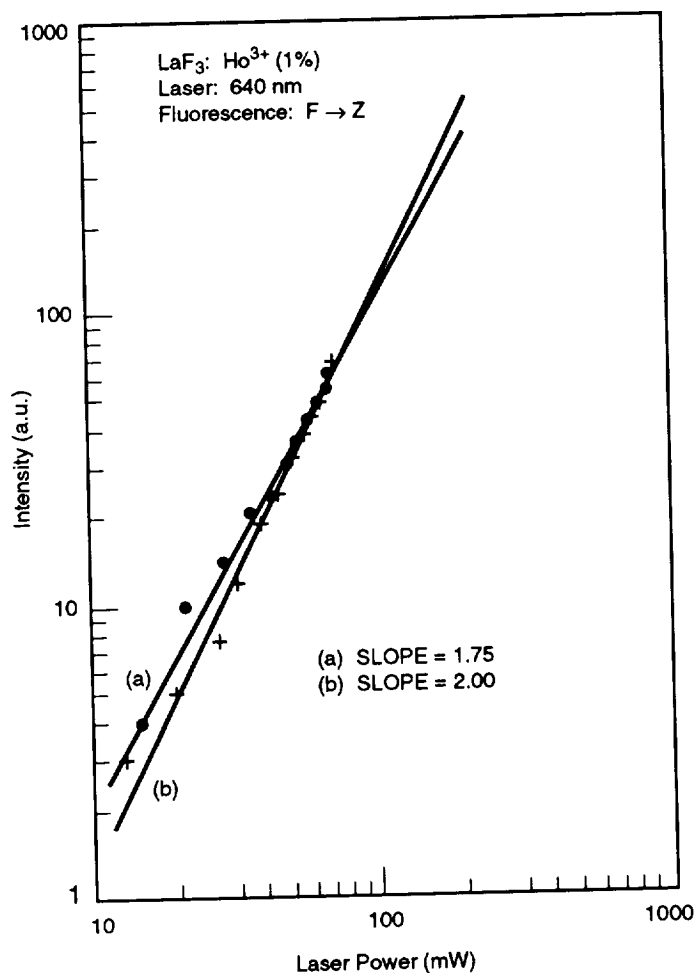


Figure 5. Power versus intensity plot of the F→Z band of LaF<sub>3</sub>:Ho<sup>3+</sup> using 640-nm laser excitation.

### LaF<sub>3</sub>:Er<sup>3+</sup>

The next system discussed is LaF<sub>3</sub>:Er<sup>3+</sup>. A partial energy level diagram of LaF<sub>3</sub>:Er<sup>3+</sup> is shown in figure 6. Using a 637-nm dye laser beam, the D level of Er<sup>3+</sup> was resonantly excited. Upconverted emissions were observed at 317-nm (P→Z), 398-nm (P→Y), 468-nm (P→A), and 540-nm (E→Z) as shown by the fluorescence spectrum (fig. 7). These transitions are shown on the energy level diagram (fig. 6) and are identified with the solid lines. Plotting P→Y fluorescence versus laser intensity yielded a gradient of 2.3, indicating that more than two photons were responsible for this emission. This was also true for P→A and P→Z fluorescence. A plot of the E→Z fluorescence versus laser intensity yielded a gradient of 1.6. This indicates that two photons were responsible for this emission.

The fluorescence spectrum of LaF<sub>3</sub>:Er<sup>3+</sup> obtained when the sample was excited with an 804-nm laser beam is shown in figure 8. Using this laser, the B level of Er<sup>3+</sup> was resonantly excited and upconverted emissions were observed at 524 nm (F→Z), 540 nm (E→Z), and 657 nm (D→Z). Since the 804-nm laser beam is resonant with the Z→B transition as well as the B→K transition, it appears that a direct stepwise two-photon excitation is responsible for the emissions.

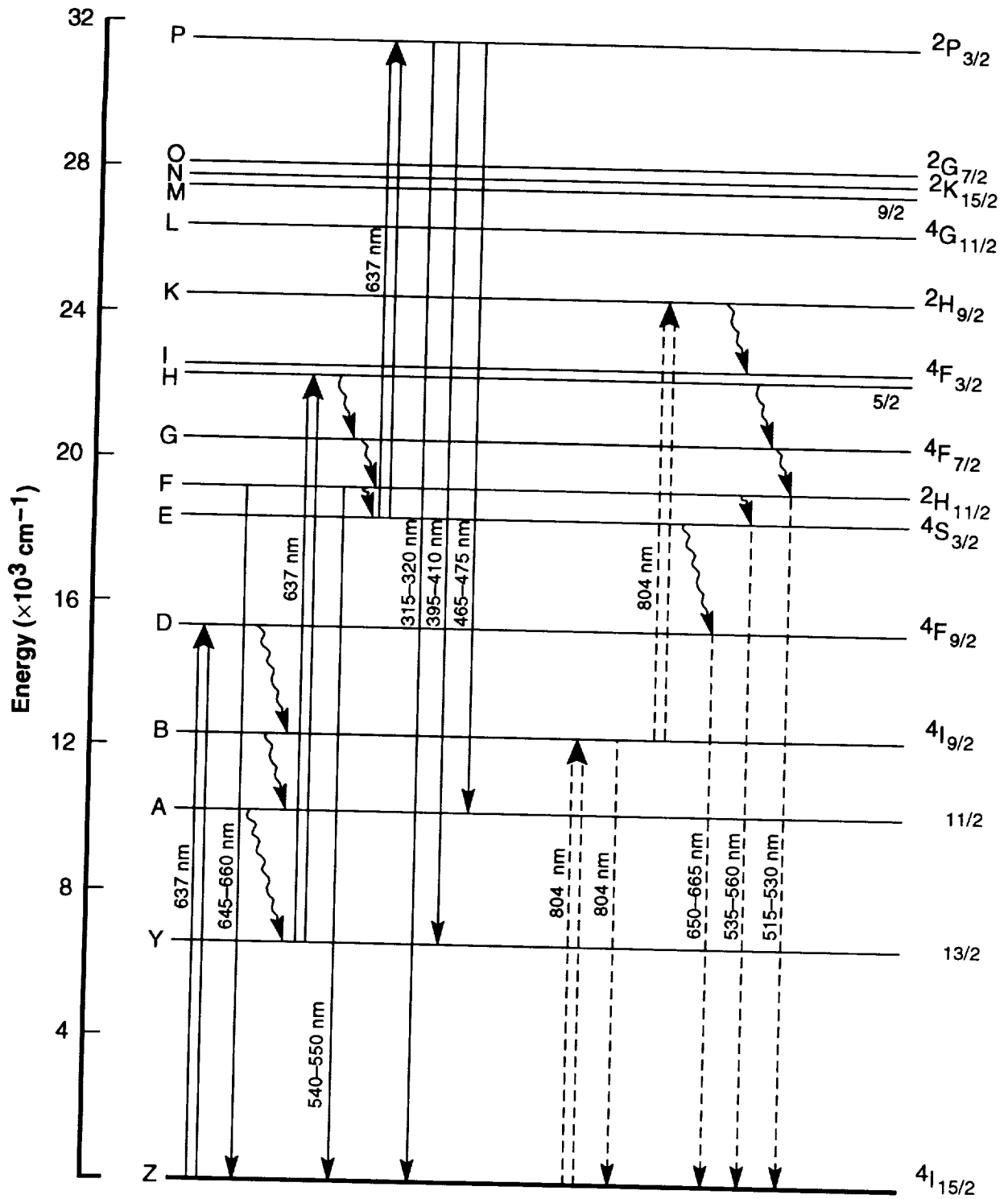


Figure 6. Partial energy level diagram of  $\text{LaF}_3:\text{Er}^{3+}$  showing observed fluorescence transitions.

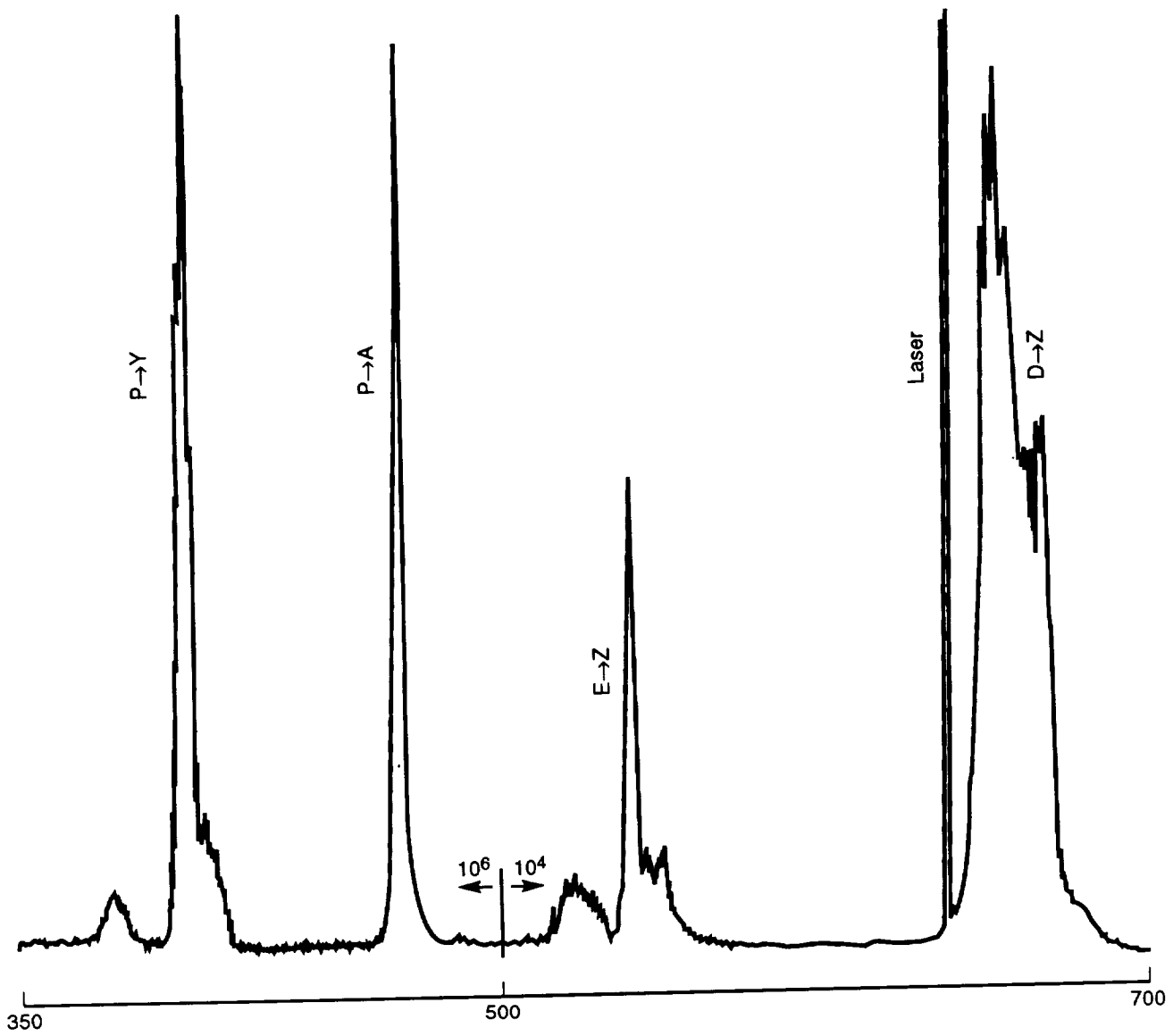


Figure 7. Fluorescence spectrum of  $\text{LaF}_3:\text{Er}^{3+}$  obtained with 637-nm laser pumping.

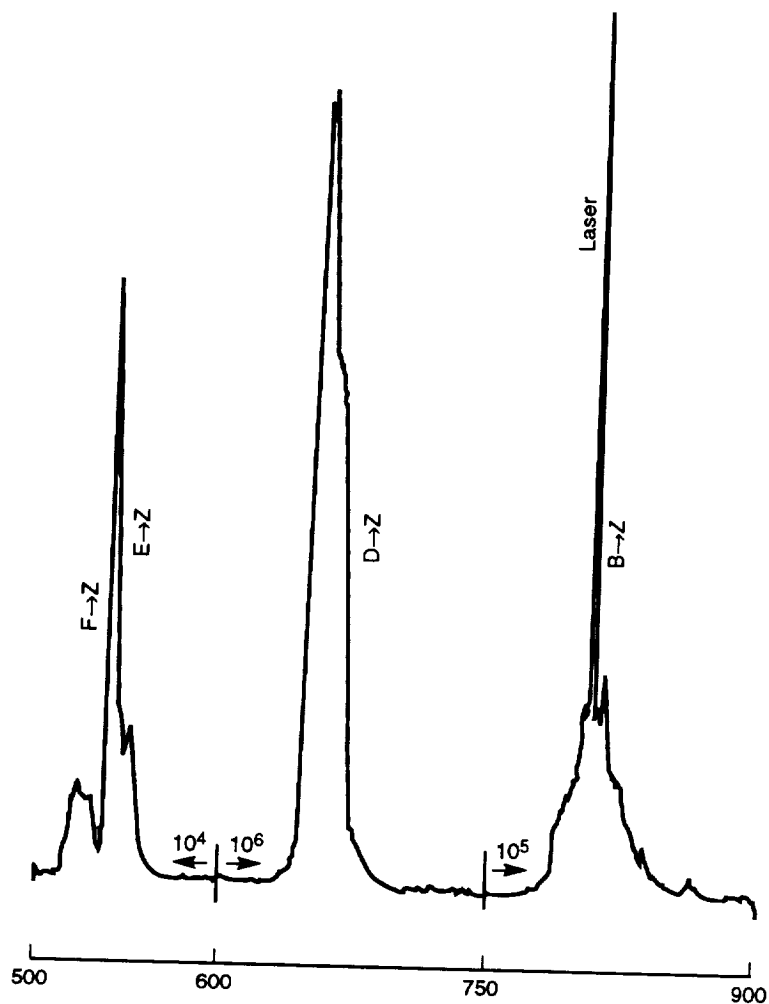


Figure 8. Fluorescence spectrum of LaF<sub>3</sub>:Er<sup>3+</sup> obtained with near infrared (804-nm) laser pumping.

### CaF<sub>2</sub>:Nd<sup>3+</sup>

The last system discussed is CaF<sub>2</sub>:Nd<sup>3+</sup>. The absorption spectrum (fig. 9) of this crystal was recorded and revealed strong peaks at 349 nm (Z→L), 521 nm (Z→E), 579 nm (Z→D), 539 nm (Z→A), and 792 nm (Z→S). From the absorption spectrum, an energy level diagram, shown in figure 10, was drawn. When the F levels of CaF<sub>2</sub>:Nd<sup>3+</sup> were resonantly excited with the 514.5-nm line of an Ar<sup>+</sup> laser, fluorescence was observed (fig. 11) at 586 nm (D→Z), 665 nm (B→Z), 788 nm (S→Z), and 861 nm (R→Z). However, when the D levels of CaF<sub>2</sub>:Nd<sup>3+</sup> were resonantly excited using the 577-nm line of a dye laser, regular fluorescence was detected as well as upconverted emissions at 360, 382, and 418 nm. The upconverted fluorescence spectrum is shown in figure 12. These transitions are identified as L→Z, L→Y, and K→Z and are shown on the energy level diagram in figure 13.

Attempts were also made to record the upconverted fluorescence of CaF<sub>2</sub>:Nd<sup>3+</sup> by pumping the sample with a near infrared laser. Unfortunately, the upconverted signals were too weak to get a good spectrum. Therefore, no further studies were done on this particular system.



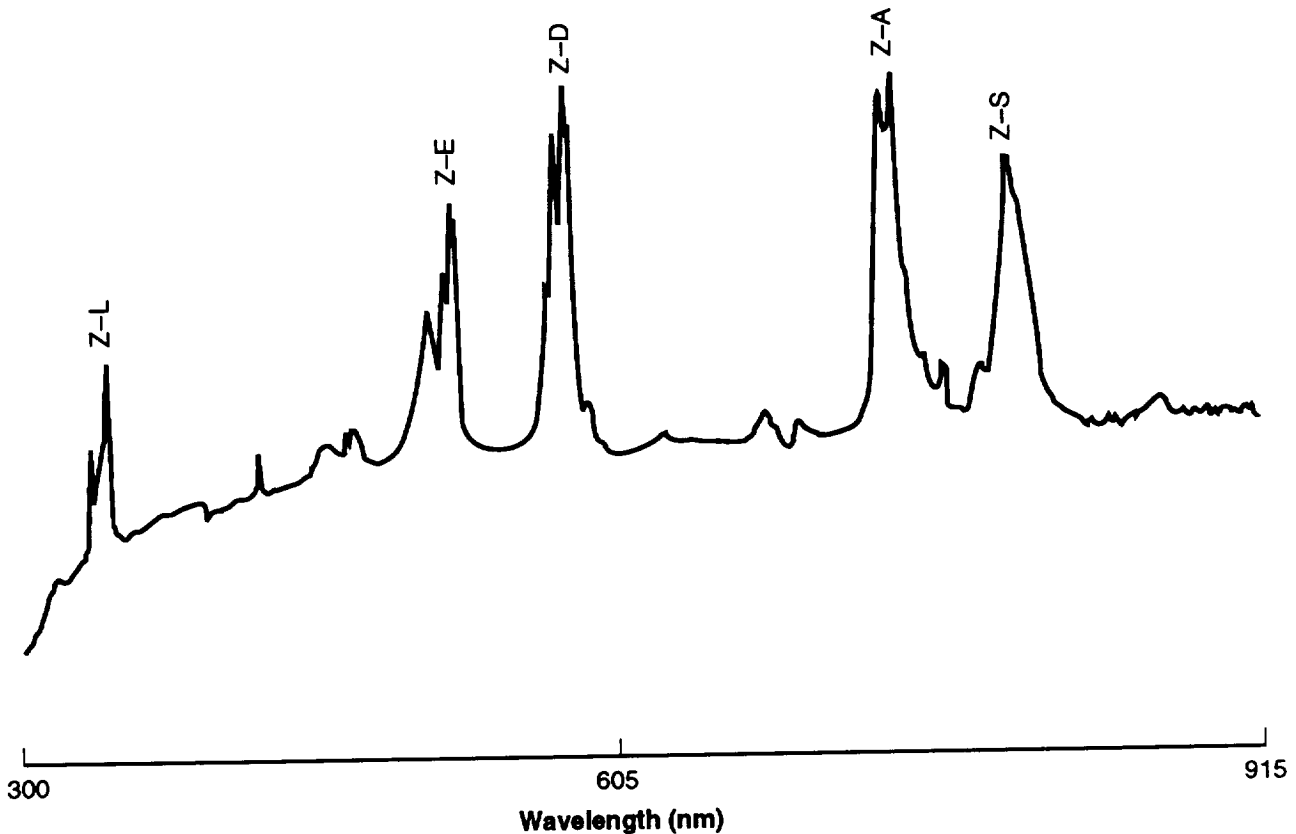


Figure 9. Absorption spectrum of CaF<sub>2</sub>:Nd<sup>3+</sup>.

## CONCLUSIONS

Of the three materials studied, LaF<sub>3</sub>:Ho<sup>3+</sup> and LaF<sub>3</sub>:Er<sup>3+</sup> would be very beneficial to the development of uncooled infrared sensors and upconversion lasers operating at room temperature. In LaF<sub>3</sub>:Ho<sup>3+</sup>, when a red laser beam and an infrared laser beam were used for excitation, green and blue emissions were detected, with bright green being visible to the naked eye in both cases. Also, when LaF<sub>3</sub>:Er<sup>3+</sup> was pumped with a red laser beam, violet, blue, and green emissions were detected. Green and red emissions were detected when the material was pumped with an infrared beam. These detected emissions were all results of energy upconversion. It was determined that sequential two-photon excitation is the dominant mechanism in upconverting energy in these systems. The upconversion efficiency of LaF<sub>3</sub>:Ho<sup>3+</sup> was found to be ~0.01 percent. The efficiency of LaF<sub>3</sub>:Er<sup>3+</sup> was not determined.

As a result of this research, a paper entitled "Energy Upconversion in LaF<sub>3</sub>:Ho<sup>3+</sup>" was presented at the Optical Society of America Annual Meeting/Ninth Interdisciplinary Laser Science Conference held in Toronto, Canada, on October 3-8, 1993. Also, a paper entitled "Near Infrared to Blue Energy Upconversion in LaF<sub>3</sub>:Ho<sup>3+</sup>" was submitted to the Journal of Optical Society of America B.

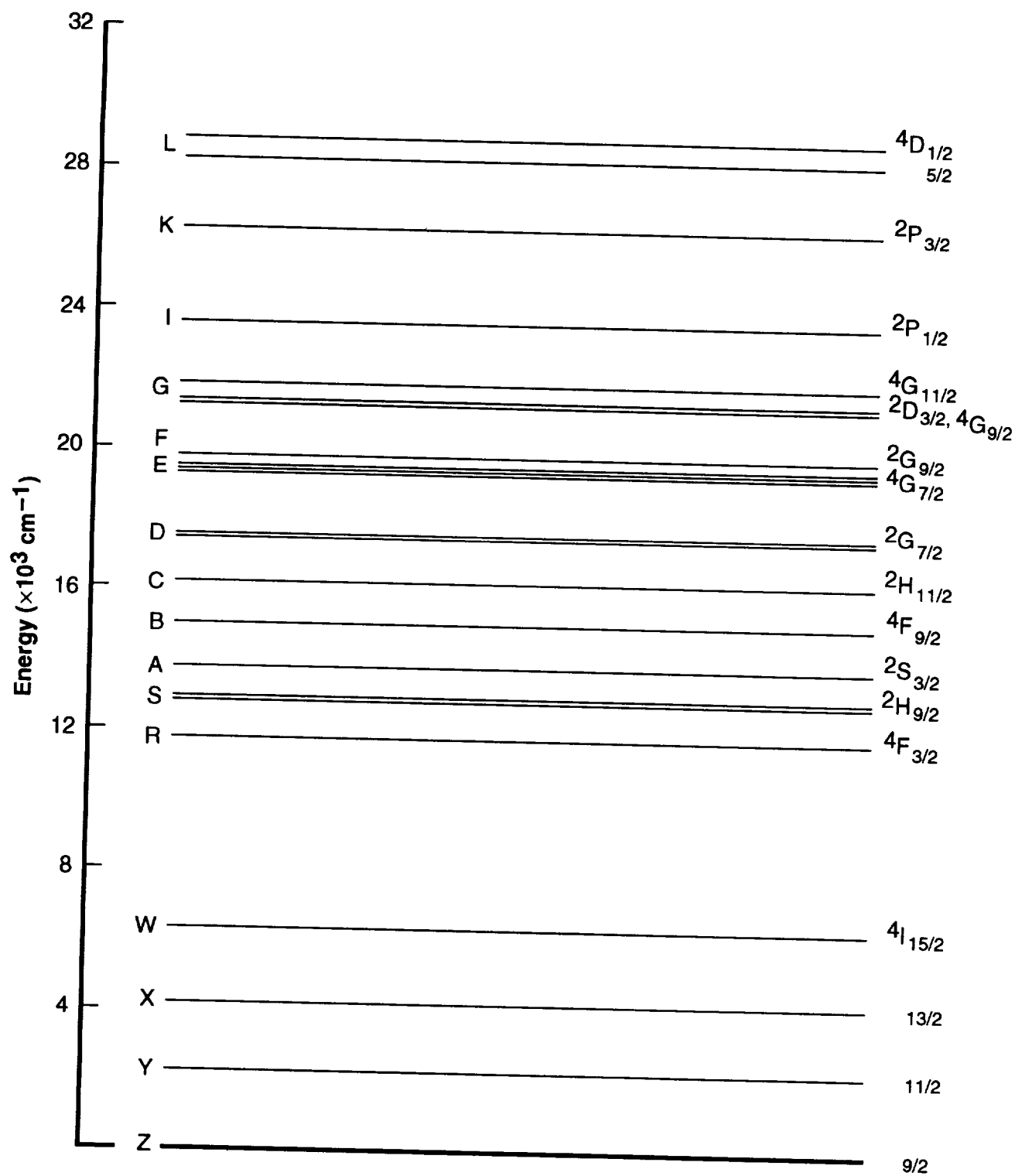


Figure 10. Partial energy level diagram of  $\text{CaF}_2:\text{Nd}^{3+}$ .

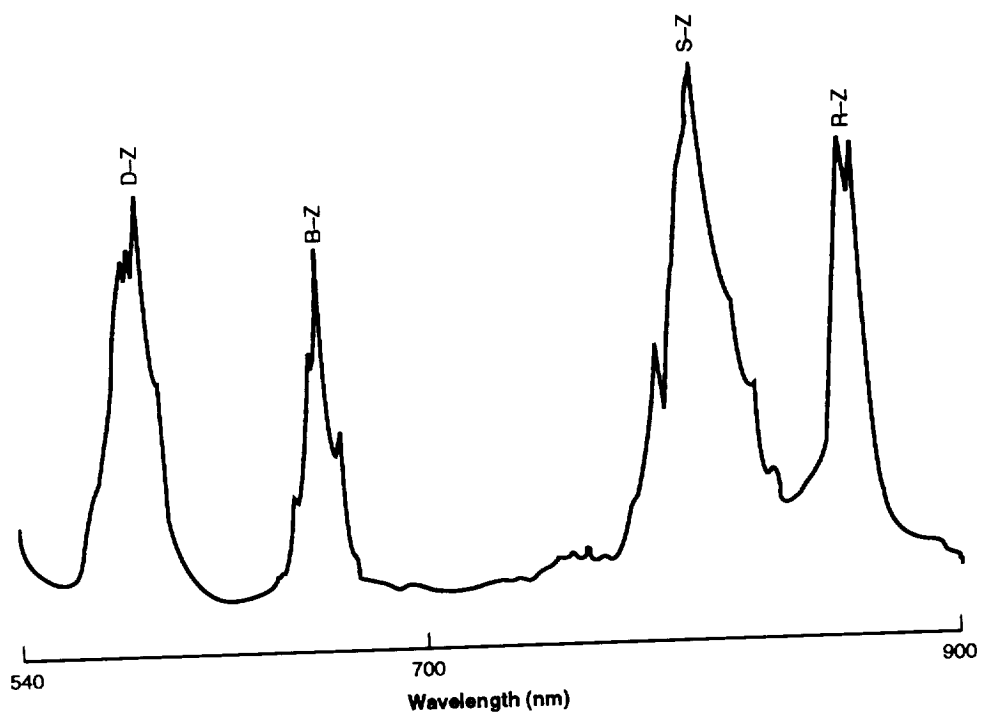


Figure 11. Fluorescence spectrum of CaF<sub>2</sub>:Nd<sup>3+</sup> obtained on excitation with an Ar<sup>+</sup> laser (514.5 nm).

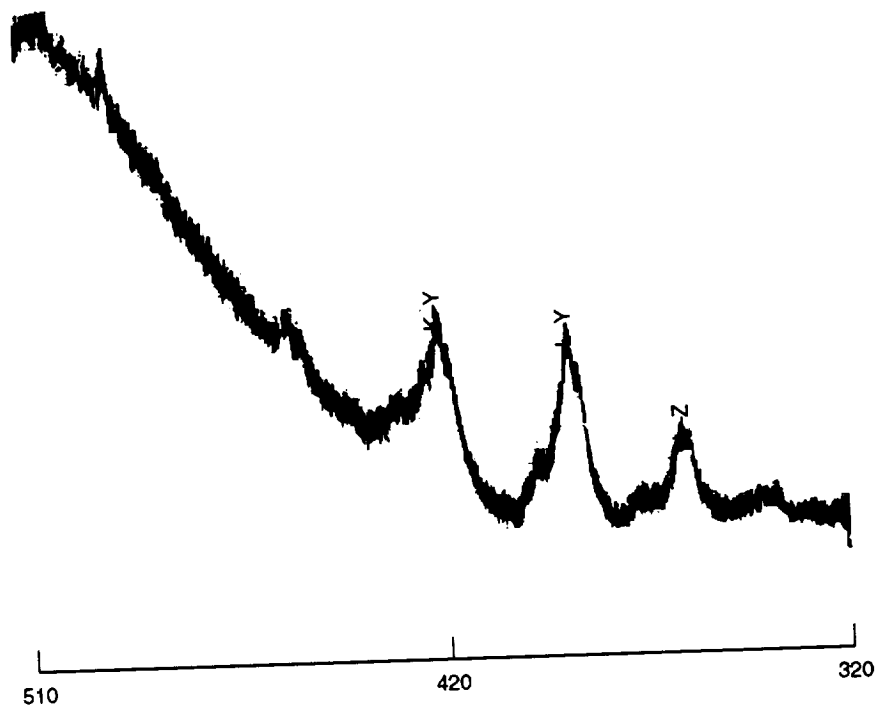


Figure 12. Upconverted fluorescence spectrum of CaF<sub>2</sub>:Nd<sup>3+</sup> obtained with dye laser (577-nm) excitation.

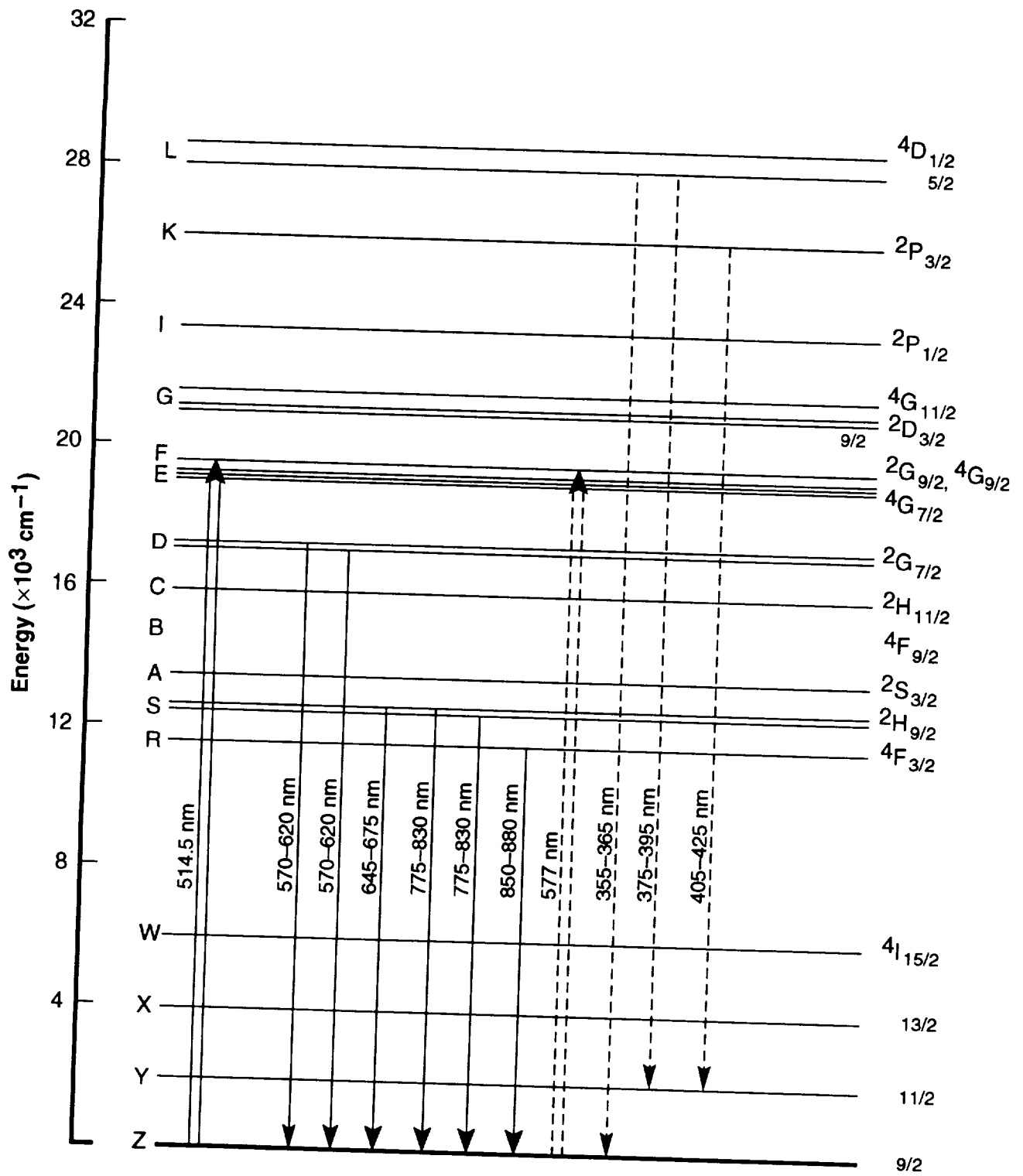


Figure 13. Partial energy level diagram of  $\text{CaF}_2:\text{Nd}^{3+}$  showing observed fluorescence transitions.


**APPROVAL**

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

  
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J.L. RANDALL  
Director, Astrionics Laboratory

