204779
18 P

NASA Technical Memorandum

(NASA-TM-108437) DEVELOPMENT OF INFRARED SENSORS USING ENERGY TRANSFER/ENERGY UPCONVERSION PROCESSES: STUDY OF LASER EXCITED FLUORESCENCE IN RARE EARTH ION DOPED CRYSTALS Final Report (NASA) 18 p

N94-24073

Unclas

G3/25 0204779

NASA TM - 108437

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

National Aeronautics and
Space Administration

George C. Marshall Space Flight Center

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
February 1994

3. REPORT TYPE AND DATES COVERED
Technical Memorandum

4. TITLE AND SUBTITLE Development of Infrared Sensors Using Energy Transfer/Energy Upconversion Processes: Study of Laser Excited Fluorescence in Rare Earth Ion Doped Crystals—Final Report: Marshall Space Flight Center Center Director's Discretionary Fund Project (CDDF) No. 91-10

5. FUNDING NUMBERS

6. AUTHOR(S)

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

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM - 108437

11. SUPPLEMENTARY NOTES

Prepared by Astrionics Laboratory, Science and Engineering Directorate.
*Alabama A&M University, Normal, Alabama 35762

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified—Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This report presents a summary of the spectroscopic study of three systems: $LaF_3:Ho^{3+}$, $LaF_3:Er^{3+}$ and $CaF_2:Nd^{3+}$. When the D levels of Ho^{3+} in LaF_3 were resonantly excited with a laser beam of 640 nm, upconverted emissions were detected from J (416 nm), F (485 nm), and E (546 nm) levels. Energy upconverted emissions were also observed from F and E levels of Ho^{3+} when the material was excited with an 800 nm near infrared laser. When the D levels of Er^{3+} in LaF_3 were resonantly excited with a laser beam of 637 nm, upconverted emissions were detected from the E (540 nm) and P (320, 400, and 468 nm) levels. Energy upconverted emissions were also observed from F, E, and D levels of Er^{3+} when the material was resonantly excited with an 804 nm near infrared laser. When the D levels of Nd^{3+} in CaF_2 were resonantly excited with a laser beam of 577 nm, upconverted emissions were detected from the L (360 and 382 nm), K (418 nm), and I (432 nm) levels. Very weak upconverted emissions were detected when this system was irradiated with a near infrared laser. The numbers in parentheses are the wavelengths of the emissions.

14. SUBJECT TERMS

$LaF_3:Ho^{3+}$, $LaF_3:Er^{3+}$ and $CaF_2:Nd^{3+}$, upconverted emissions

15. NUMBER OF PAGES
19

16. PRICE CODE
NTIS

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unlimited

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

DEFINITION OF SYMBOLS

Symbol	Definition
$LaF_3:Ho^{3+}$	Lanthanum fluoride with triply ionized holmium
$LaF_3:Er^{3+}$	Lanthanum fluoride with triply ionized erbium
$CaF_2:Nd^{3+}$	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 CaF_2 and 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.

$LaF_3:Ho^{3+}$

A partial energy level diagram of 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 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 ~1.1×10^{-4}.

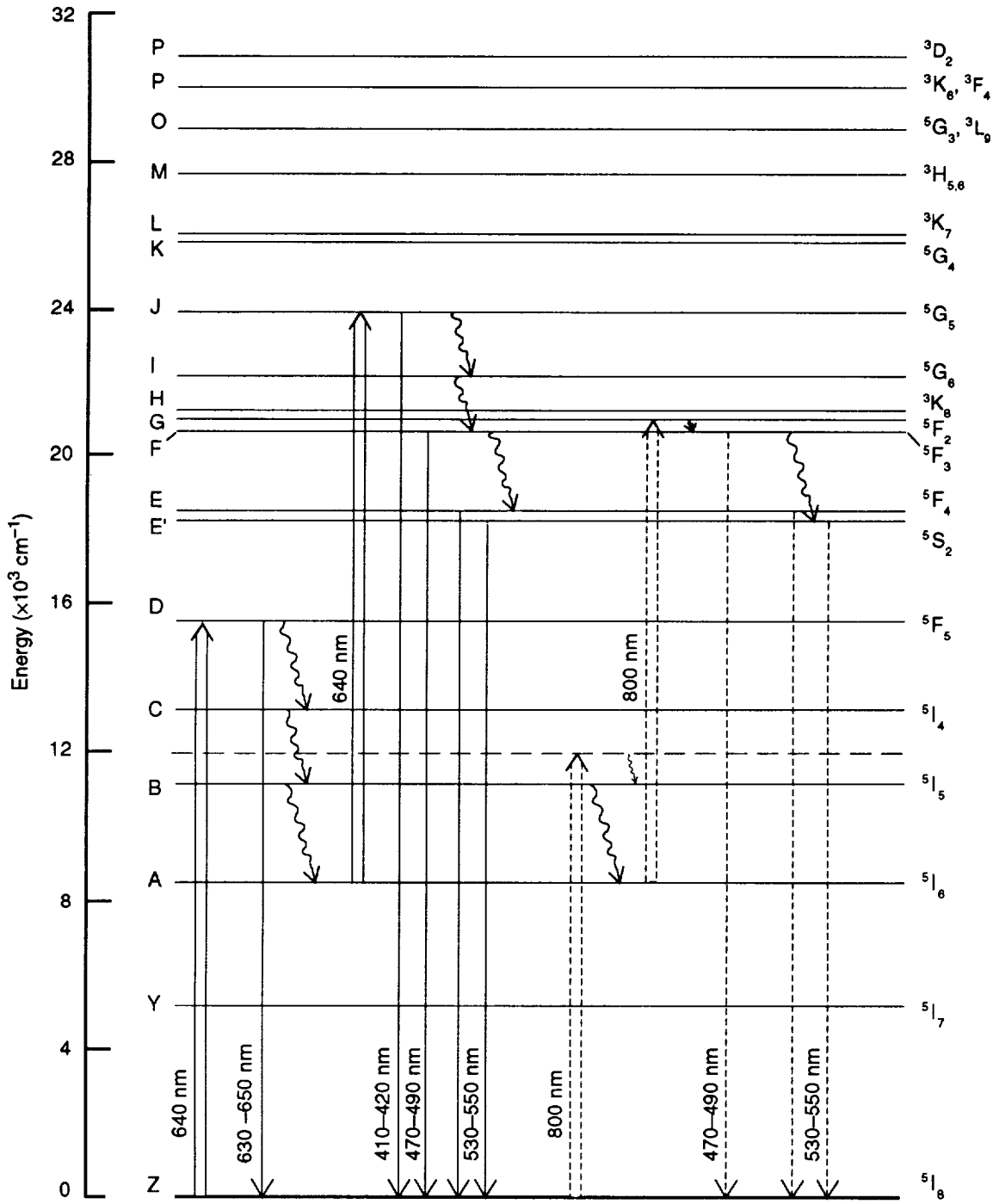

Figure 1. Partial energy level diagram of $LaF_3:Ho^{3+}$ showing observed fluorescence transitions.

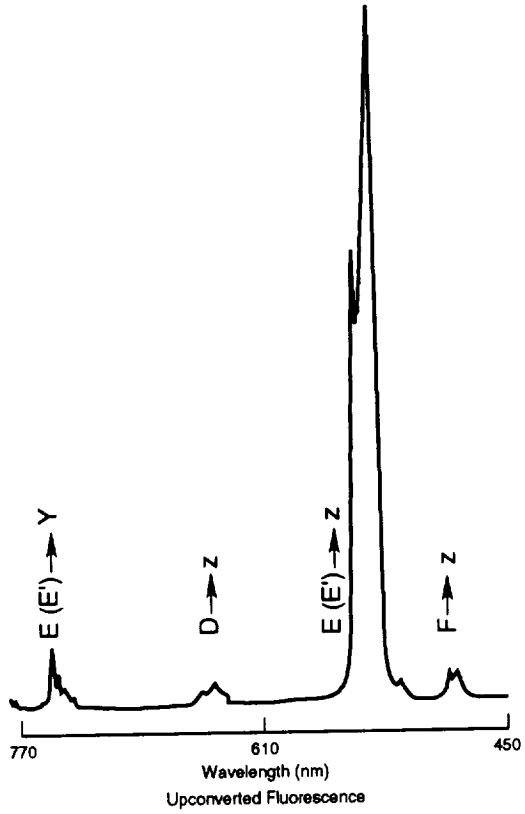

Figure 2. Upconverted fluorescence spectrum of $LaF_3:Ho^{3+}$ obtained by pumping the material with a near infrared laser (800 nm).

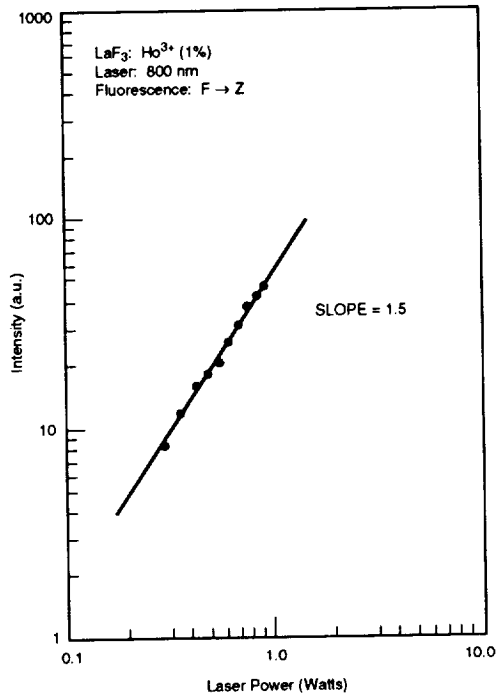

Figure 3. Power versus intensity plot of the F→Z band of $LaF_3:Ho^{3+}$ using 800-nm laser excitation.

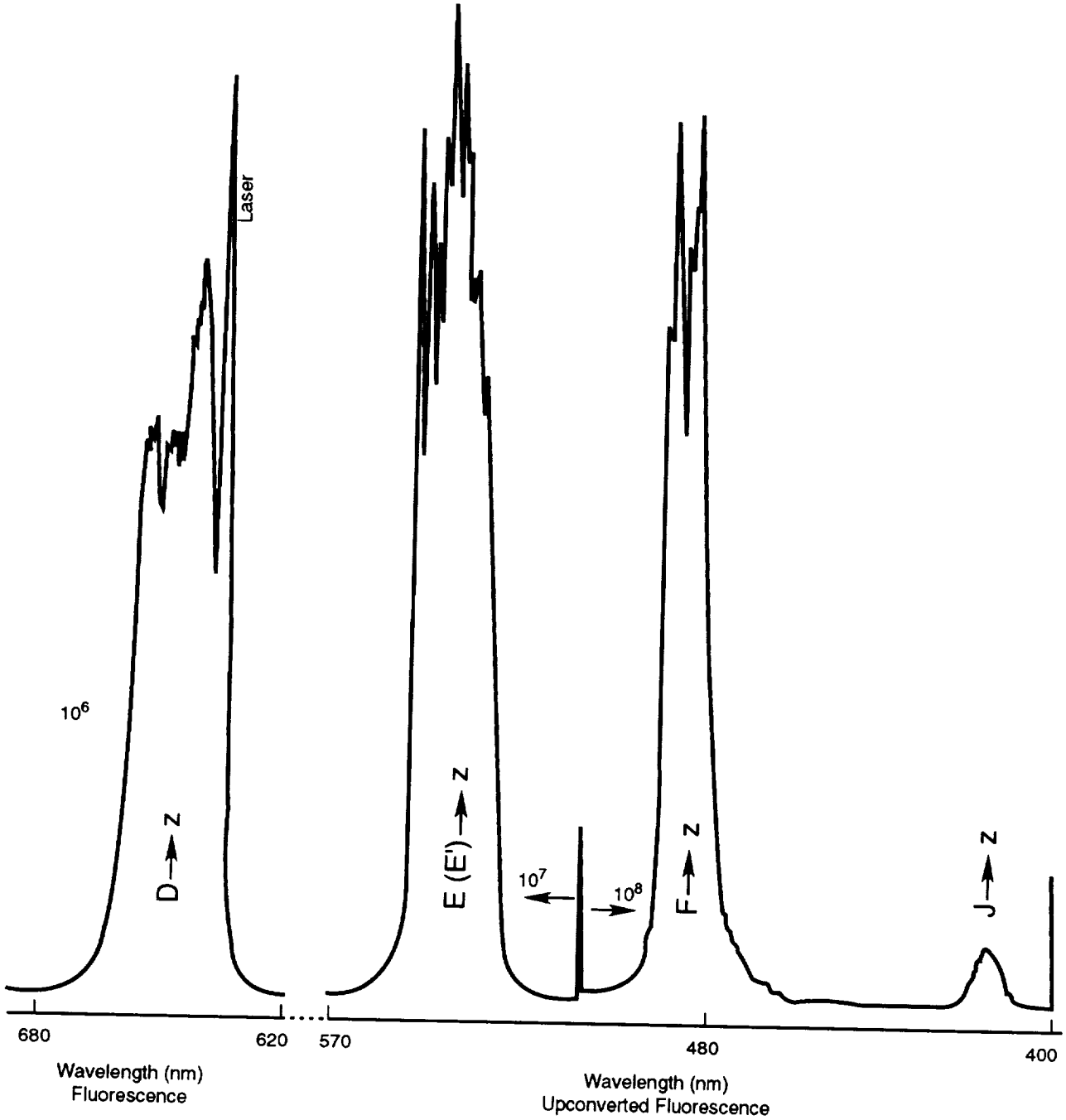

Figure 4. Fluorescence spectrum of $LaF_3:Ho^{3+}$ using 640-nm laser excitation.

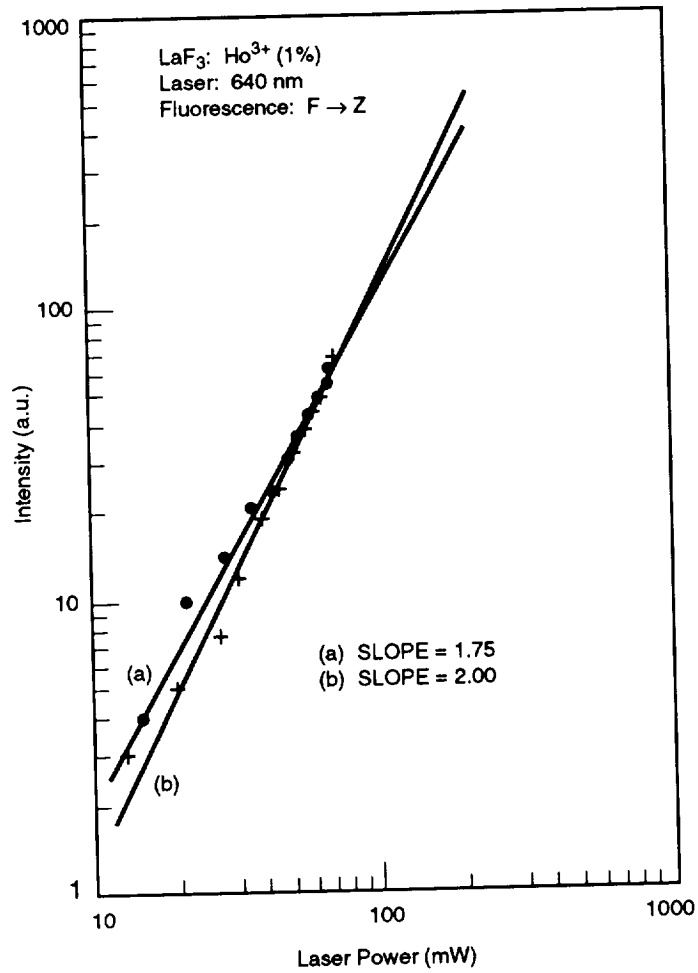

Figure 5. Power versus intensity plot of the F→Z band of $LaF_3:Ho^{3+}$ using 640-nm laser excitation.

$LaF_3:Er^{3+}$

The next system discussed is $LaF_3:Er^{3+}$. A partial energy level diagram of $LaF_3:Er^{3+}$ is shown in figure 6. Using a 637-nm dye laser beam, the D level of Er^{3+} 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 $LaF_3:Er^{3+}$ 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^{3+} 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.

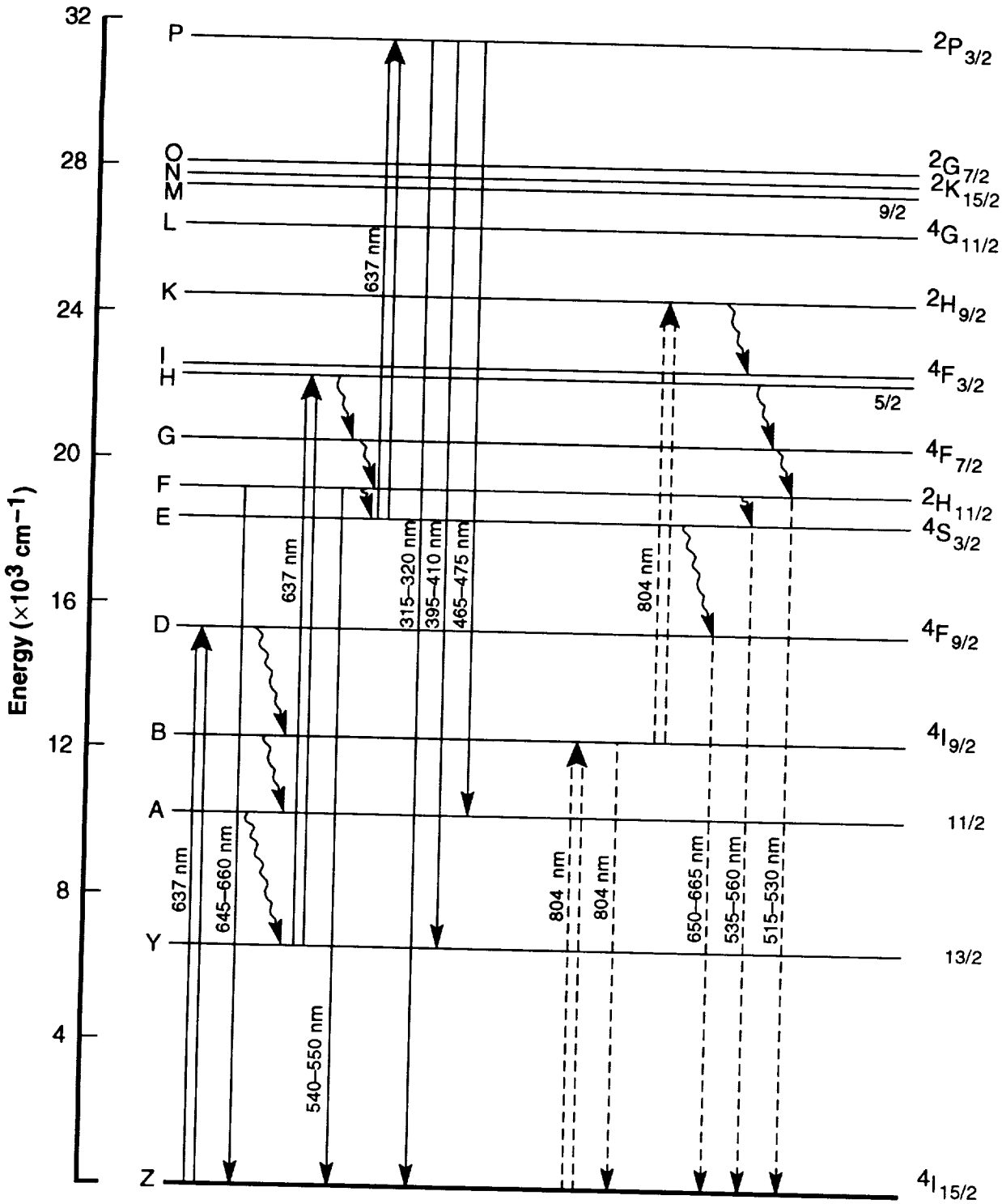

Figure 6. Partial energy level diagram of $LaF_3:Er^{3+}$ showing observed fluorescence transitions.

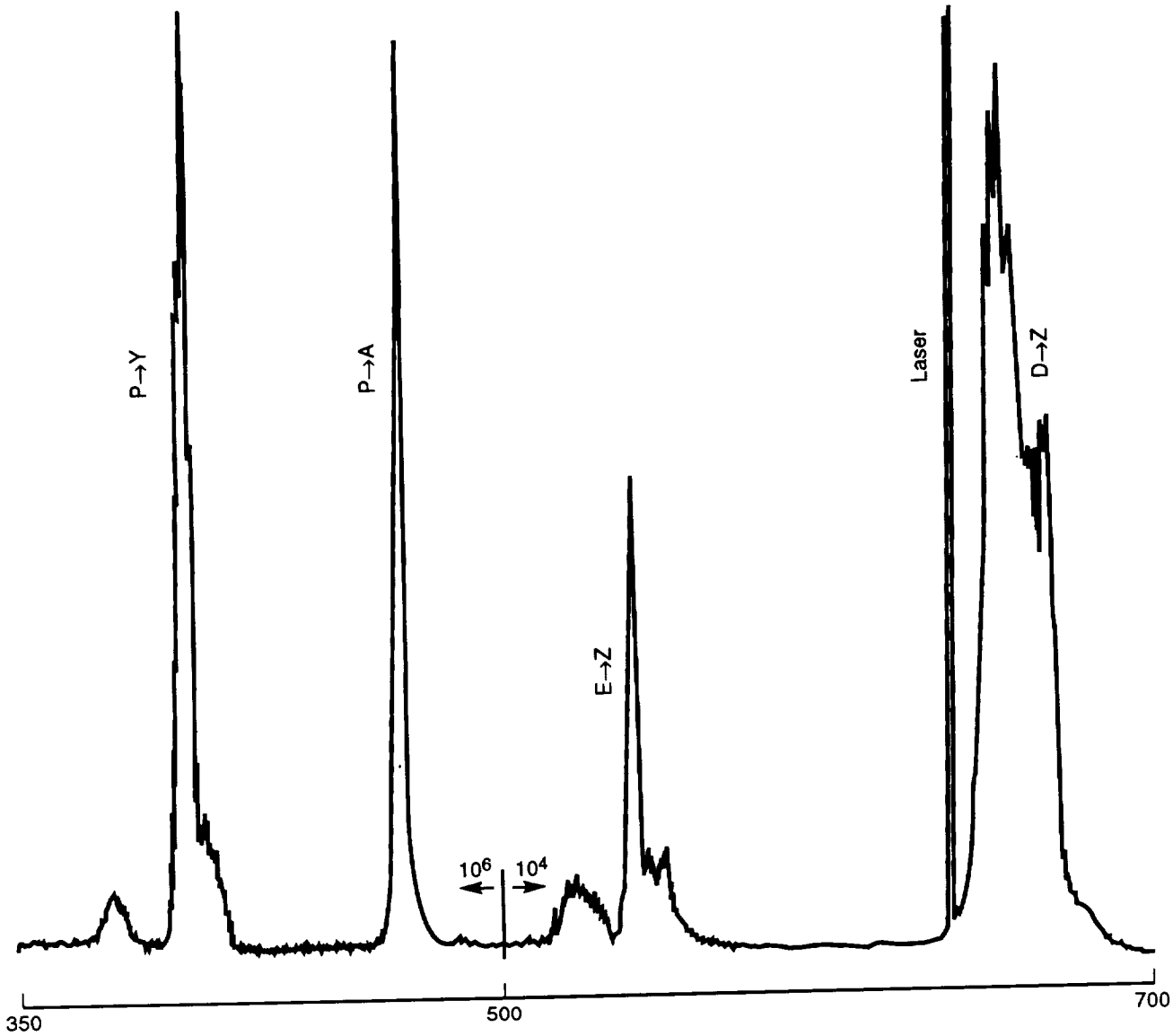

Figure 7. Fluorescence spectrum of $LaF_3:Er^{3+}$ obtained with 637-nm laser pumping.

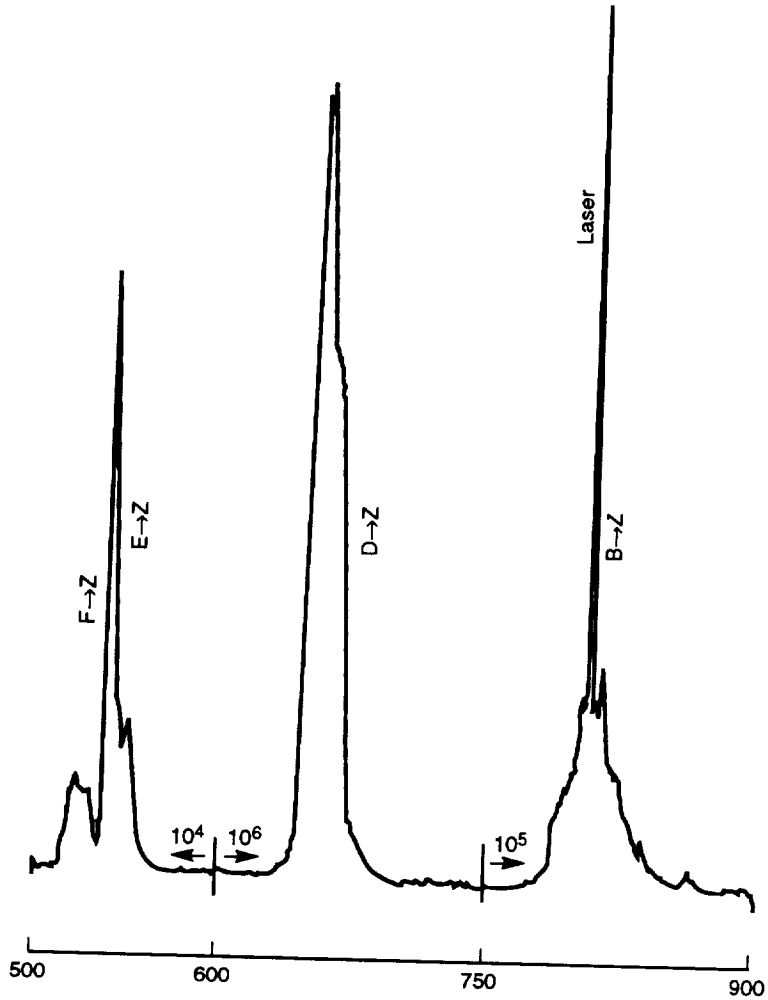

Figure 8. Fluorescence spectrum of $LaF_3:Er^{3+}$ obtained with near infrared (804-nm) laser pumping.

$CaF_2:Nd^{3+}$

The last system discussed is $CaF_2:Nd^{3+}$. 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 $CaF_2:Nd^{3+}$ were resonantly excited with the 514.5-nm line of an Ar^+ 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 $CaF_2:Nd^{3+}$ 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 $CaF_2:Nd^{3+}$ 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.

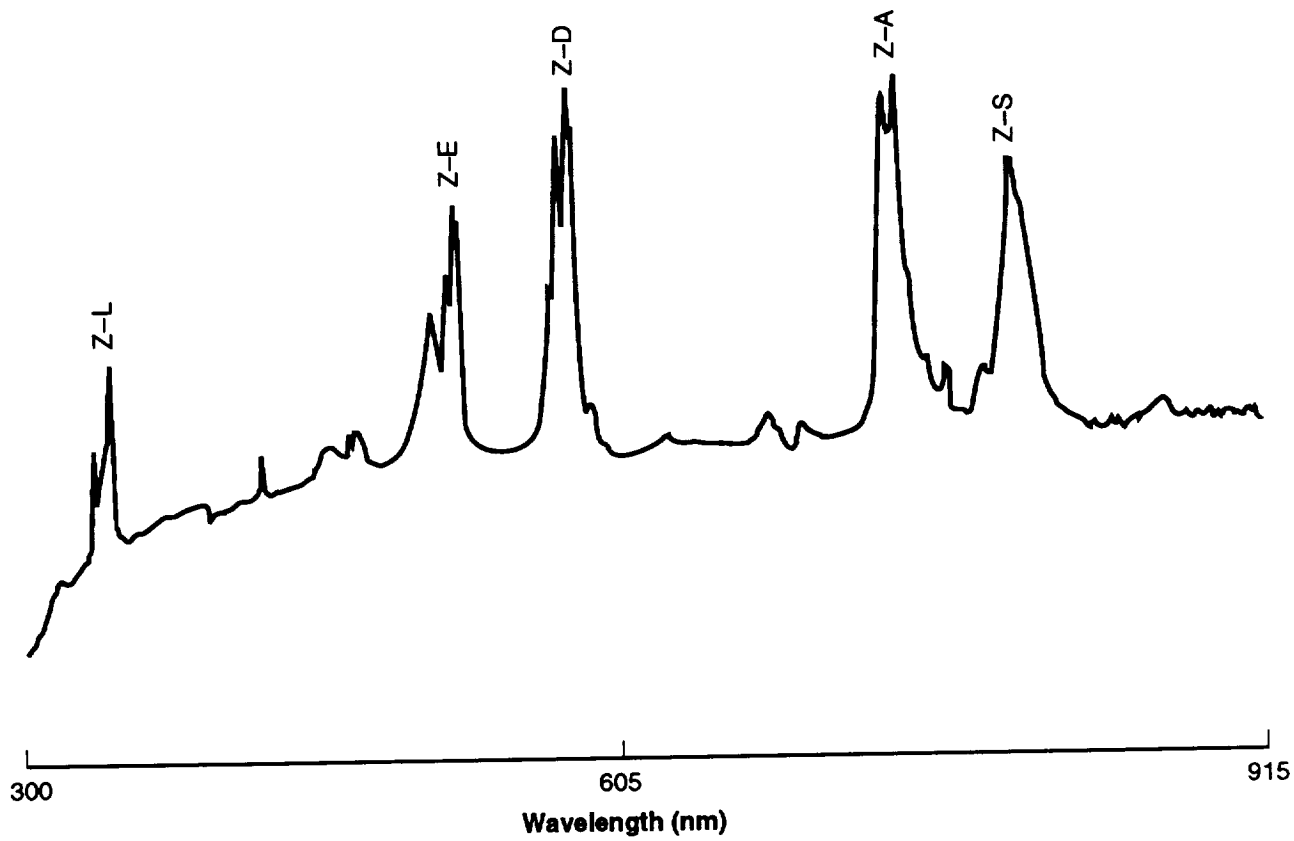

Figure 9. Absorption spectrum of $CaF_2:Nd^{3+}$.

CONCLUSIONS

Of the three materials studied, $LaF_3:Ho^{3+}$ and $LaF_3:Er^{3+}$ would be very beneficial to the development of uncooled infrared sensors and upconversion lasers operating at room temperature. In $LaF_3:Ho^{3+}$, 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 $LaF_3:Er^{3+}$ 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 $LaF_3:Ho^{3+}$ was found to be ~0.01 percent. The efficiency of $LaF_3:Er^{3+}$ was not determined.

As a result of this research, a paper entitled "Energy Upconversion in $LaF_3:Ho^{3+}$" 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 $LaF_3:Ho^{3+}$" was submitted to the Journal of Optical Society of America B.

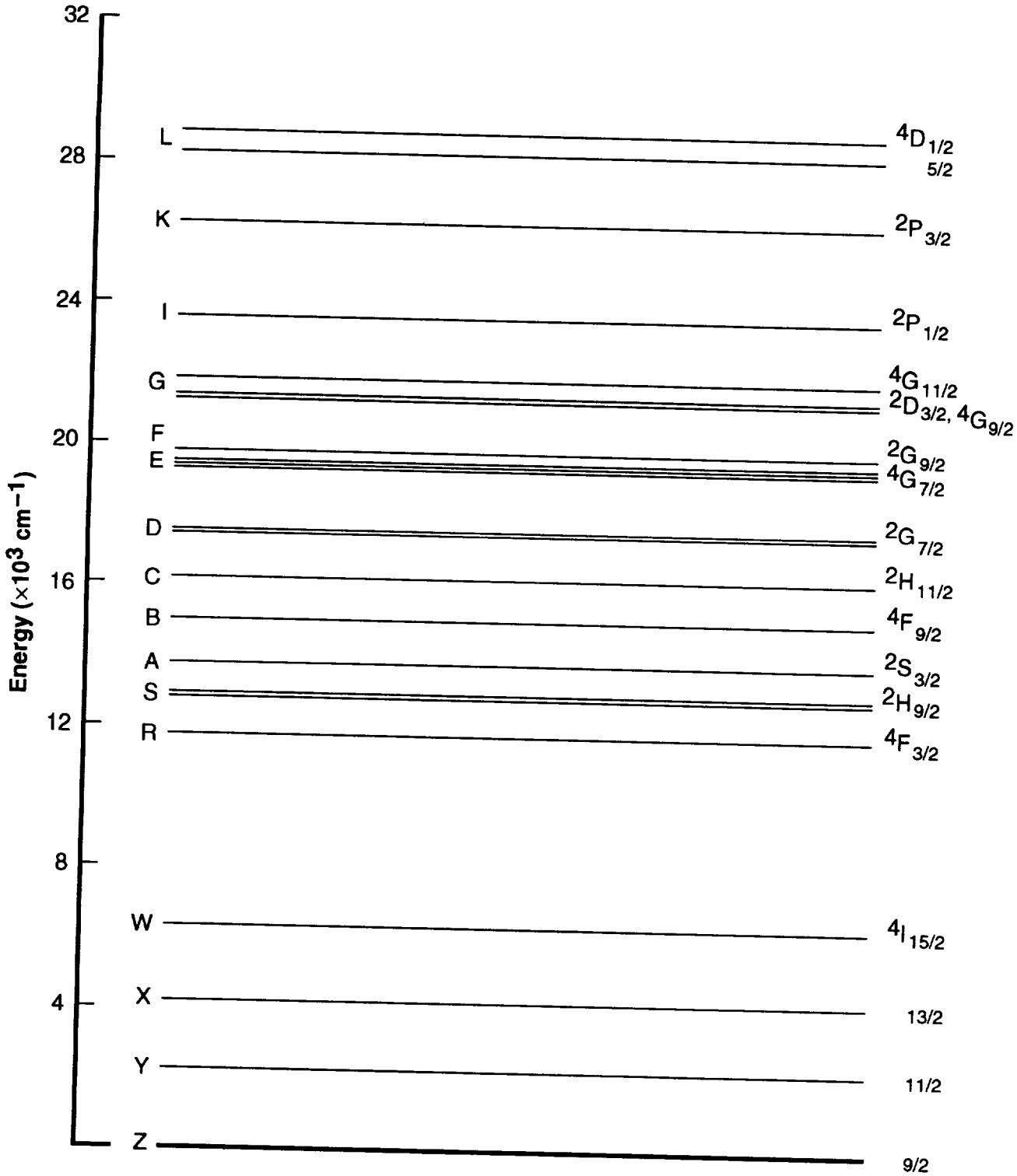

Figure 10. Partial energy level diagram of $CaF_2:Nd^{3+}$.

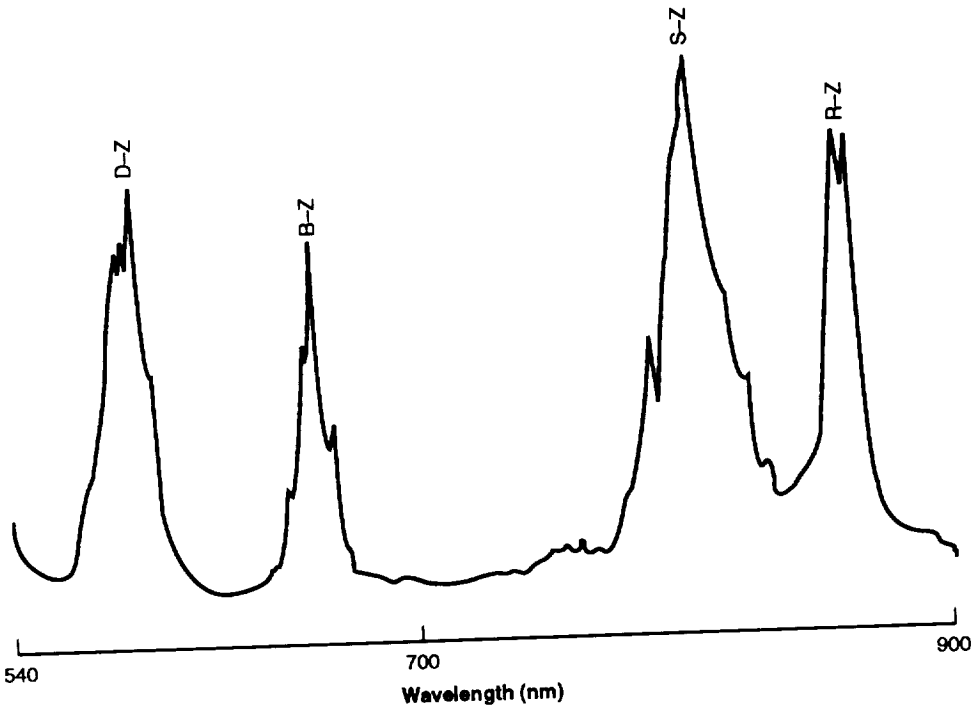

Figure 11. Fluorescence spectrum of $CaF_2:Nd^{3+}$ obtained on excitation with an Ar^+ laser (514.5 nm).

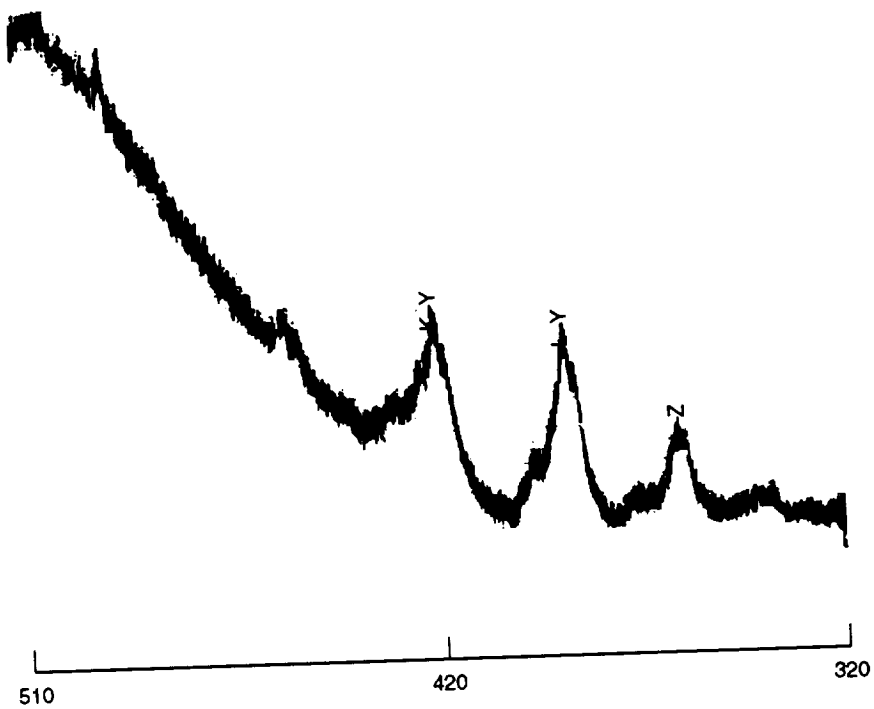

Figure 12. Upconverted fluorescence spectrum of $CaF_2:Nd^{3+}$ obtained with dye laser (577-nm) excitation.

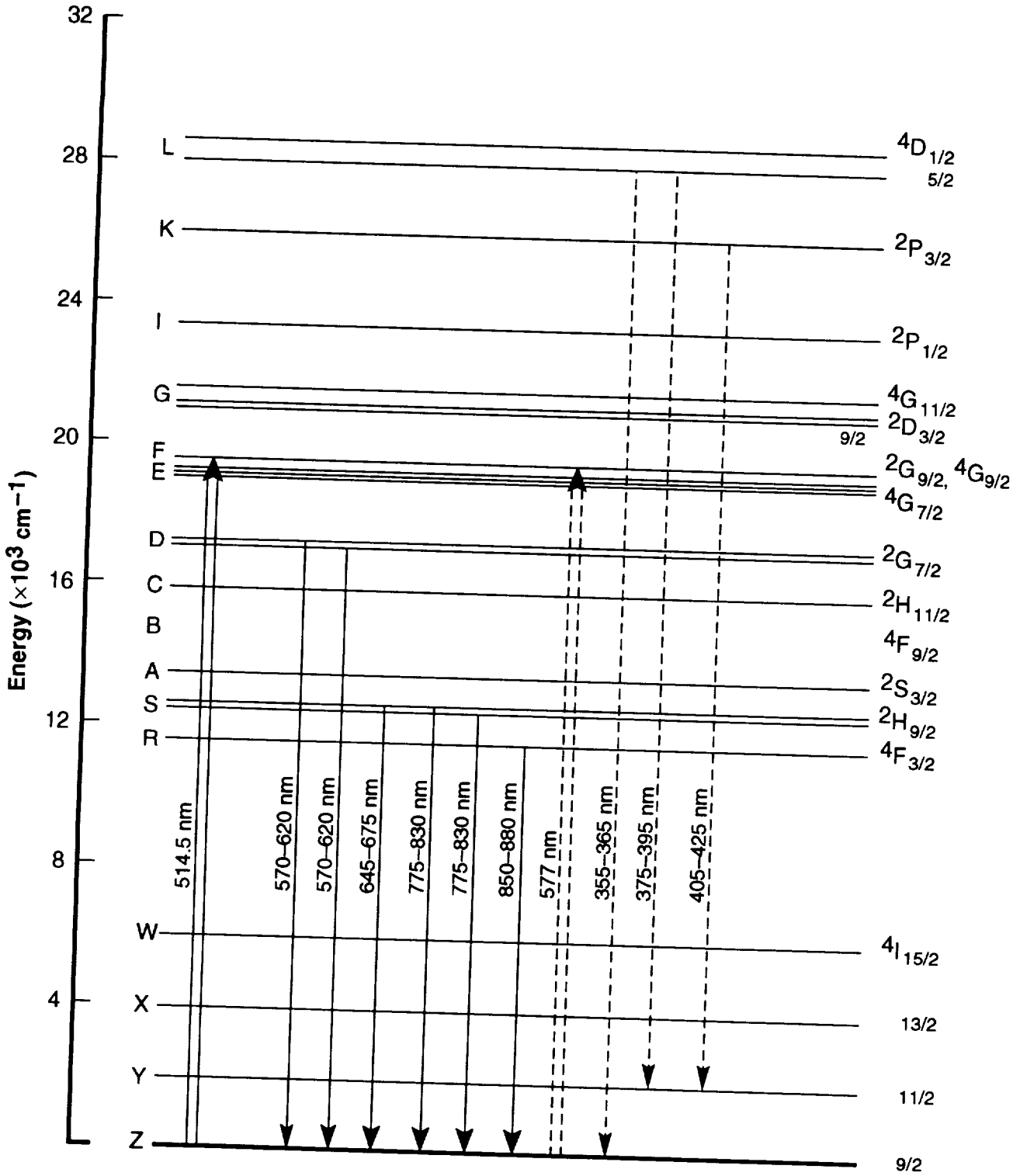

Figure 13. Partial energy level diagram of $CaF_2:Nd^{3+}$ showing observed fluorescence transitions.

APPROVAL

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

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.

J.L. RANDALL
Director, Astrionics Laboratory

☆ U.S. GOVERNMENT PRINTING OFICE 1994 533–108 /00013