

Influence of Temperature on the Green-to-Blue Up-Conversion Emission from U^{4+} Ion in Single-Crystal Cs_2ZrCl_6 ¹

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The blue emission from $U^{4+}(5f^2)$ ion doped into a Cs_2ZrCl_6 single crystal under green light ($19,436\text{ cm}^{-1}$) excitation has been observed and characterized. Five blue emission bands for the intra $5f\ ^1I_6 \rightarrow ^3H_4$ ($19,700$, $20,010$, and $20,280\text{ cm}^{-1}$) and $^3P_2 \rightarrow ^3H_4$ ($20,700$ and $20,970\text{ cm}^{-1}$) U^{4+} transitions have been observed. The up-conversion efficiencies for the 1I_6 and 3P_2 emissions have been estimated as a function of temperature; that for 3P_2 emission increases with increasing temperature. We suggest that this result is due to an increasing population of the 3P_2 level caused by thermal excitation of U^{4+} ions in the 1I_6 level. © 1995 Academic Press, Inc.

INTRODUCTION

Single-crystal Cs_2ZrCl_6 is an interesting host material for luminescence studies of tetravalent actinide ions; it exhibits an optical window from $30,000$ to 4000 cm^{-1} . Crystals of Cs_2ZrCl_6 are easily grown, and they can accommodate relatively high concentrations of tetravalent actinide ions (1–5). In addition, Cs_2ZrCl_6 has a low phonon energy ($<330\text{ cm}^{-1}$) which is very important in reducing the nonradiative quenching of the tetravalent actinide ion's fluorescence. Tetravalent actinide ions generally possess a larger spin-orbit coupling constant and crystal field than do the trivalent lanthanide ions, which reduces the energy gaps between the excited electronic states and makes actinide ions in general less fluorescent than lanthanide ions. We chose to study the optical properties of U^{4+} ion doped into a Cs_2ZrCl_6 single crystal for several reasons. The $5f^2$ configuration of the U^{4+} ion provides

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experimental features in sufficient detail to be suitable for theoretical analysis and to constitute a useful basis for extending the interpretation of optical spectra in condensed media. Also, U^{4+} ion is easy to stabilize in selected optically clear hosts and its inherent radioactivity is quite low. On the other hand, the oscillator strength (10^{-4}) of U^{4+} ion is much larger than that of U^{3+} (10^{-5}) and Pr^{3+} (10^{-6}) ions (6). We have observed, for the first time, relatively strong blue up-conversion emission from $U^{4+}(5f^2)$ ion in a $Cs_2ZrCl_6:U^{4+}$ single crystal under green light ($19,436\text{ cm}^{-1}$) excitation (7). This up-conversion emission requires a two-photon absorption by the dopant U^{4+} ions in their ground state.

The purpose of this work was to obtain the fluorescence efficiency of this blue up-conversion emission in the $Cs_2ZrCl_6:U^{4+}$ single crystal. The temperature dependence of the up-conversion efficiency has also been studied.

EXPERIMENTAL DETAILS

The Cs_2ZrCl_6 host crystal is very hygroscopic, so care must be taken in its preparation and handling in order to prevent contamination by moisture. The UCl_4 dopant material was purified by loading the nominally pure starting material into a silica tube and pumping it down to $\sim 20\ \mu\text{m Hg}$ at 650°C to remove any moisture or excess HCl . The tube was then sealed, and the UCl_4 was sublimated at 510°C from one end of the tube to the other. A crystal of Cs_2ZrCl_6 was grown by the Bridgman technique from a melt containing a stoichiometric mixture of $ZrCl_4$ and $CsCl$ with 1 wt% UCl_4 .

Visible and near-IR absorption spectra were measured with a Cary Model 14H scanning spectrophotometer converted by On-Line Instrument Systems (OLIS) for data acquisition and analysis by an IBM-compatible computer. The $21,837\text{ cm}^{-1}$ (457.9 nm) and $19,436\text{ cm}^{-1}$ (514.5 nm) lines from a Coherent Model 300 argon-ion laser were used as the excitation sources. The luminescence spectra

were recorded with a Ramanor Model HG.2S spectrophotometer (Jobin-Yvon/Instruments SA) having a resolution of 0.5 cm^{-1} at 514 nm . The collected light was detected by a photon counting system, which employed a cooled photomultiplier tube (Hamamatsu 636) and a multichannel analyzer (Nicolet 1170) interfaced with an AT personal computer using "Spectra Calc" software (Galactic Industries Corp.).

The Raman spectrum was recorded with the same Ramanor spectrophotometer. A krypton laser (Spectra Physics Model 164) served as the light source. After filtering by the grating monochromator, 30 mW of laser power at a wavelength of 647.1 nm reached the sample. The scattered light was collected at 90° from the incident laser excitation. The collected light was then dispersed by a monochromator and detected by a cooled photomultiplier tube (Hamamatsu 636).

The intensity of the exciting light was monitored with a Coherent Model 240 power meter.

RESULTS AND DISCUSSION

The emission spectra from the $\text{Cs}_2\text{ZrCl}_6:\text{U}^{4+}$ single-crystal sample upon $21,837 \text{ cm}^{-1}$ excitation (excited directly into the 3P_2 level) at different temperatures in the wavenumber region $19,500$ to $21,500 \text{ cm}^{-1}$ are shown in Fig. 1. These three blue emissions, centered at $19,700$, $20,010$, and $20,280 \text{ cm}^{-1}$, are attributed to the $^1I_6 \rightarrow ^3H_4$ transitions in the U^{4+} ion. Furthermore, two weaker blue emissions are observed at $20,700$ and $20,970 \text{ cm}^{-1}$ which correspond to the $^3P_2 \rightarrow ^3H_4$ transitions in the U^{4+} ion. It should be noted that when the single-crystal sample is warmed from 200 to 460 K , the blue emission from the

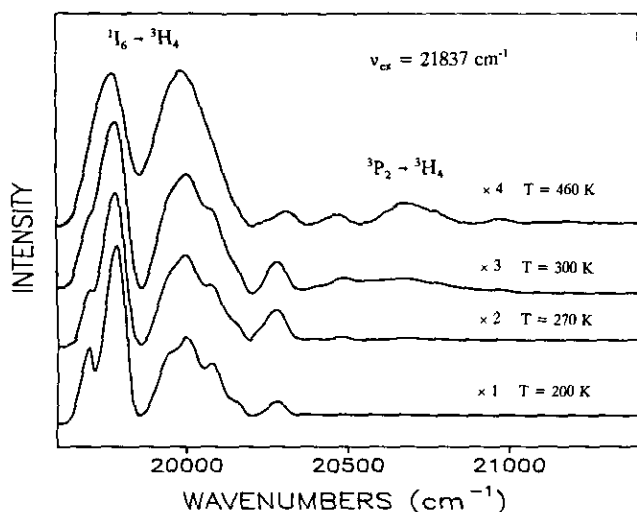


FIG. 1. Emission spectrum from U^{4+} ion in a Cs_2ZrCl_6 single-crystal sample doped with $1 \text{ wt}\%$ UCl_4 at different temperatures under $21,837 \text{ cm}^{-1}$ light excitation.

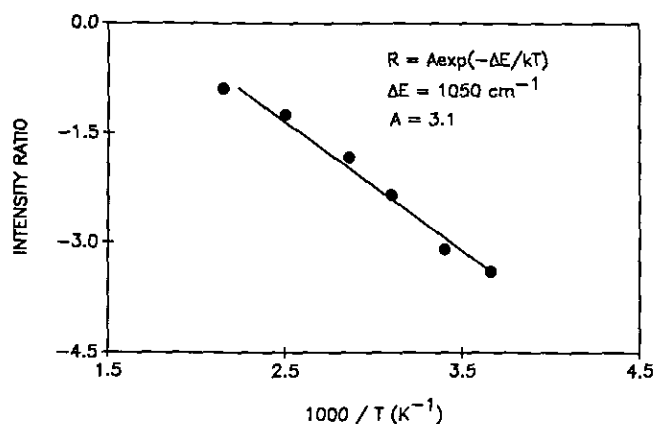


FIG. 2. Logarithm of the ratio of the integrated intensities of the $^3P_2 \rightarrow ^3H_4$ and $^1I_6 \rightarrow ^3H_4$ emissions as a function of inverse absolute temperature ($10^3/T$).

3P_2 level is observed with greater intensity. We suggest that this increased emission from the 3P_2 level with increasing temperature results from its increased thermal population from the 1I_6 level. An analysis based on a simple three-level system comprising the 3P_2 (level 3), 1I_6 (level 2), and 3H_4 (level 1) levels predicts that thermalization of the 3P_2 level can be expressed by the equation (8, 9)

$$I_3/I_2 = A \exp(-E_{32}/kT) \quad (1)$$

where

$$A = (W_{R3}g_3\hbar\omega_3)/(W_{R2}g_2\hbar\omega_2) \quad (2)$$

and I_3 and I_2 are the emission intensities of the $^3P_2 \rightarrow ^3H_4$ and $^1I_6 \rightarrow ^3H_4$ transitions in the U^{4+} ion, respectively, W_{R2} and W_{R3} are the radiative transition probabilities for the two transitions level 2 \rightarrow level 1 and level 3 \rightarrow level 1, g_2 and g_3 are the respective level degeneracies ($2J + 1$), and $\hbar\omega_2$ and $\hbar\omega_3$ are the photon energies of the respective transitions. E_{32} is the energy gap between the 3P_2 and 1I_6 levels and k is Boltzmann's constant. The validity of Eq. [1] is checked by recording the emission spectrum at various temperatures and plotting the logarithm of the ratio of the intensities I_3/I_2 vs $10^3/T$ as shown in Fig. 2. The solid line is a least-squares fit to the data over the 200 – 460 K temperature range investigated. It can be seen that a good fit to Eq. (1) is obtained. The plot of $\ln(I_3/I_2)$ vs $10^3/T$ exhibits a single exponential decrease over this temperature range with the energy gap E_{32} equal to 1050 cm^{-1} . This agrees with the absorption and emission energy difference between the 3P_2 and 1I_6 levels.

The up-conversion emission spectra from the same sample under $19,436 \text{ cm}^{-1}$ excitation (excited directly into the 3P_1 level) at 200 and 300 K in the wavenumber range

19,500 to 21,500 cm^{-1} is given in Fig. 3. Because the blue up-conversion emissions are from the same excited states of U^{4+} ion, the shape, position, and relative intensity of each emission band are consistent with those obtained in a one-photon excitation of U^{4+} ion, but when the temperature is below 200 K, the 3P_2 blue emission is not observed. In addition, the intensity of the 1I_6 up-conversion emission decreases with increasing temperature while that of the 3P_2 emission band increases with increasing temperature. For example, when the temperature increases from 200 to 300 K, the intensity of the 1I_6 emission decreases by a factor of 1.6, while the 3P_2 emission intensity increases by a factor of 2.3.

The intensities of the 1I_6 and 3P_2 emissions show quadratic dependence on the excitation intensity under green light (19,436 cm^{-1}) excitation (7). For example, the slopes of the curves have been found to be 1.9, 2.0, and 2.2 for the 20,010, 20,280, and 20,700 cm^{-1} emissions from this sample, respectively.

In order to estimate the fluorescence efficiency (η) of the blue up-conversion emission from U^{4+} ion at different temperatures upon 19,436 cm^{-1} light excitation, without having at hand an absolutely calibrated optical system, we compared the emission from our $Cs_2ZrCl_6:U^{4+}$ sample to a "standard" sample under the same excitation conditions of 40 mW/cm^2 incident light. Details of the technique used to determine η have been described previously (11, 12).

The temperature dependence of the up-conversion efficiencies of the 1I_6 and 3P_2 blue emissions from the single-crystal $Cs_2ZrCl_6:U^{4+}$ sample under green light (19,436 cm^{-1}) excitation is plotted in Fig. 4. Associated numerical values are listed in Table 1. It is noted that the up-conver-

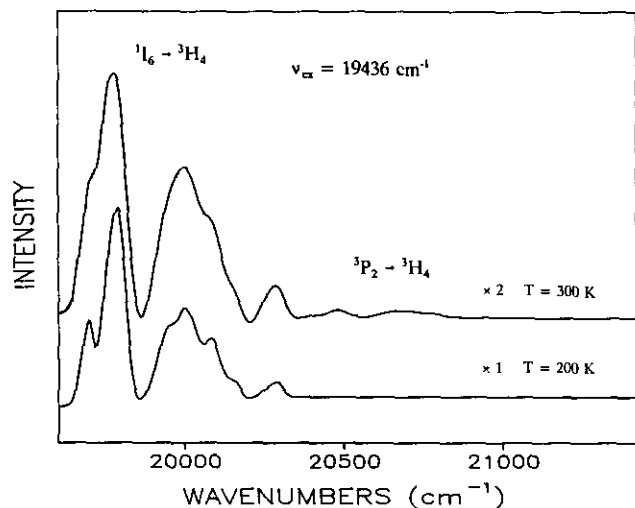


FIG. 3. Up-conversion emission spectrum from U^{4+} ion in the Cs_2ZrCl_6 sample at 200 and 300 K under green light (19,436 cm^{-1}) excitation.

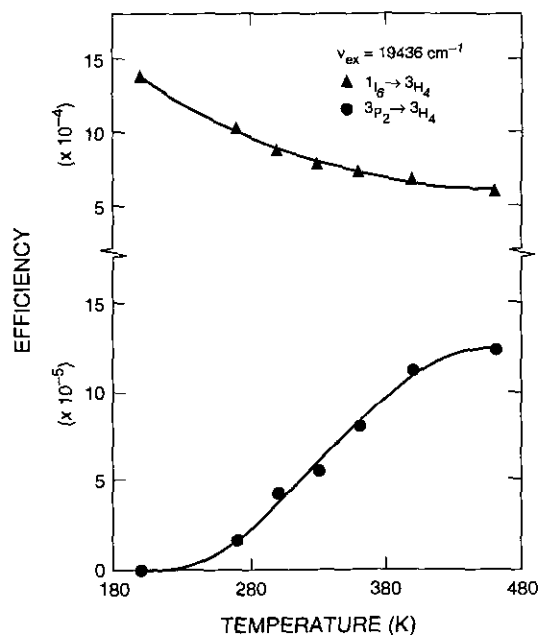


FIG. 4. Temperature dependence of the blue up-conversion efficiencies for the (\blacktriangle) $^1I_6 \rightarrow ^3H_4$ and (\bullet) $^3P_2 \rightarrow ^3H_4$ emissions in a $Cs_2ZrCl_6:U^{4+}$ single crystal under green light (19,436 cm^{-1}) excitation.

sion efficiency of the $^1I_6 \rightarrow ^3H_4$ emission decreases with increasing temperature; at 200 K it is about 2.4 times greater than that at 460 K. In contrast, the up-conversion efficiency of the $^3P_2 \rightarrow ^3H_4$ emission increases by 7 times when the temperature is increased from 270 to 460 K.

The phonon energy for the $Cs_2ZrCl_6:U^{4+}$ single crystal is obtained from its Raman spectrum (see Fig. 5) recorded at room temperature under 647.1 nm light excitation. As can be seen the maximum phonon energy of this single crystal is about 330 cm^{-1} .

TABLE 1
Up-Conversion Emission Efficiencies of U^{4+} Ion Obtained from a Cs_2ZrCl_6 Single Crystal Containing 1 wt% UCl_4 at Various Temperatures under Green Light (19,436 cm^{-1}) at 40 mW/cm^2 Incident Power

T (K)	$^1I_6 \rightarrow ^3H_4$ $\eta (\times 10^{-4})$	$^3P_2 \rightarrow ^3H_4$ $\eta (\times 10^{-5})$
200	13.90	~0
270	10.40	1.70
300	8.78	4.20
330	7.88	5.30
360	7.30	7.84
400	6.70	11.00
460	5.90	12.10

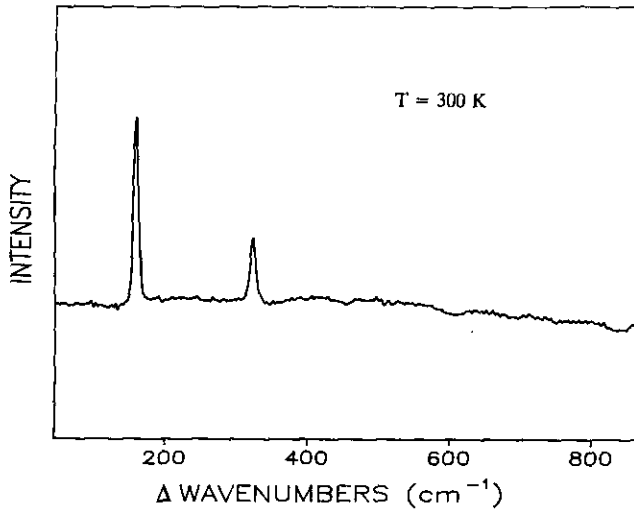


FIG. 5. Raman spectrum of a $\text{Cs}_2\text{ZrCl}_6:\text{U}^{4+}$ single crystal at room temperature under 647.1 nm light scattering.

Five, blue up-conversion emission bands centered at 19,700, 20,010, and 20,280 cm^{-1} for the $^1I_6 \rightarrow ^3H_4$ U^{4+} transitions and at 20,700 and 20,970 cm^{-1} for the $^3P_2 \rightarrow ^3H_4$ U^{4+} transitions have been observed under 19,436 cm^{-1} light excitation; the shape, position, and relative intensity of the emission bands are consistent with those obtained in a one-photon excitation of the U^{4+} ion (13). In addition, the intensities of these emissions depend quadratically on the excitation light intensity. This means that these up-conversion processes involve a two-photon absorption (9, 12). In the first photon absorption step, U^{4+} ions are excited directly into the 3P_1 level ((1) in Fig. 6). Then they may relax nonradiatively to the 3F_2 level. A second 19,436 cm^{-1} photon absorption by these excited U^{4+} ions raises them to the 3P_2 and 1I_6 levels, respectively ((2) in Fig. 6), following loss of some energy via a nonradiative relaxation process. The observed blue emissions result from the $^3P_2 \rightarrow ^3H_4$ and $^1I_6 \rightarrow ^3H_4$ U^{4+} transitions. This up-conversion mechanism is referred to as an excited states absorption (ESA) process. On the other hand, when the temperature is below 200 K, the $^3P_2 \rightarrow ^3H_4$ blue emission is not observed. This suggests that the emission from the 3P_2 level is probably due to its population via thermal excitation of U^{4+} ions in the 1I_6 level.

The highest fluorescence efficiency (η) of the main blue up-conversion emission ($^1I_6 \rightarrow ^3H_4$ transitions) was obtained at the lowest temperature studied, i.e., 200 K. We suggest that the decrease in this blue up-conversion emission efficiency between 200 and 460 K is caused by an increase in the nonradiative relaxation rate, a reduction in the up-conversion excitation efficiency and of the effective emission cross section (due to thermal line broadening), and/or a redistribution of level populations within the manifolds (14).

The efficiency (η) of the up-conversion process depends sensitively on the radiative quantum efficiency (η_Q) of the excited state. η_Q is obtained from

$$\eta_Q = W_R / (W_R + W_{NR}), \quad [3]$$

where W_R and W_{NR} are the radiative and nonradiative rates of relaxation of the state (15, 16). On the basis of a single-configuration coordinate model (8), the temperature dependence of the nonradiative rate is given by

$$W_{NR} = W_{NR}(0) [\exp(\hbar\omega/kT) / (\exp(\hbar\omega/kT) - 1)]^p \quad [4]$$

where $W_{NR}(0)$ is the low-temperature multiphonon emission rate, $\hbar\omega$ is the phonon energy, and p is the number of phonons emitted in the transition. Combining Eqs. [3] and [4], the radiative quantum efficiency can be expressed as

$$\eta_Q = [1 + B(1 - \exp(-\hbar\omega/kT))^{-p}]^{-1} \quad [5]$$

where

$$B = W_{NR}(0) / W_R. \quad [6]$$

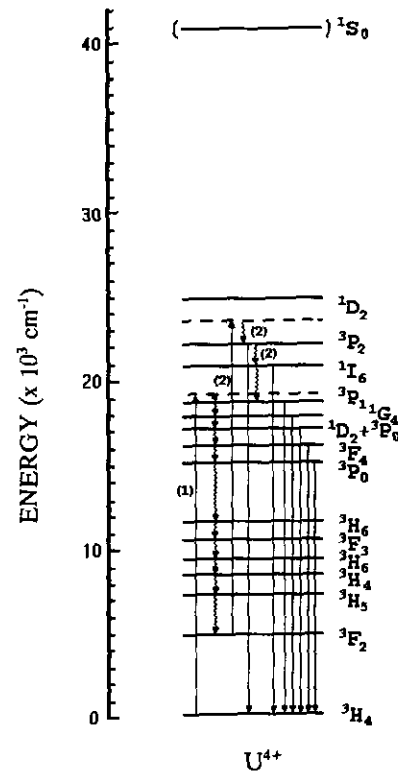


FIG. 6. Schematic free-ion energy level diagram for U^{4+} ion with some excitation and emission processes.

From Eq. [5], when the temperature increases, the $(1 - \exp(-\hbar\omega/kT))^{-p}$ term increases, and therefore, η_Q decreases. Our experimental observations are in agreement with this theoretical result.

The fluorescence efficiency of the other blue up-conversion emission (${}^3P_2 \rightarrow {}^3H_4$ transitions) increases with increasing temperature. As stated earlier, we suggest that this behavior results from the increased thermal population of the 3P_2 level from the 1I_6 level. Direct excitation of the U^{4+} ion as a function of temperature produces the same results (see Fig. 1).

In summary, we have observed relatively strong blue up-conversion emission from the $U^{4+}(5f^2)$ ion in a Cs_2ZrCl_6 single crystal under green light ($19,436\text{ cm}^{-1}$) excitation. This result suggests that such a single crystal might find applications where it is desired to convert green into blue light. The up-conversion efficiencies of the ${}^1I_6 \rightarrow {}^3H_4$ and ${}^3P_2 \rightarrow {}^3H_4$ emissions have been estimated as a function of temperature. That from the 1I_6 level decreases with increasing temperature, presumably due to an increase in its nonradiative decay rate. In contrast, that from the 3P_2 level increases over the temperature range studied, and we postulate that this behavior results from an increasing thermal population of this 3P_2 level from the 1I_6 level which lies about 1000 cm^{-1} below it.

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