

## Up Conversion Process in $U^{4+}$ -Doped $ThBr_4$ and $ThCl_4$

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Infrared excitation of tetravalent uranium in thorium tetrahalides produces a strong emission in the red region at room temperature. The experimental results show that a two-photon mechanism is involved. Below liquid nitrogen temperature the conversion efficiency increases and an extra green emission appears. © 1986 Academic Press, Inc.

### Introduction

Up conversion processes in solids have been extensively investigated during the last 20 years. It can occur both between identical and different ions through energy transfer or in one single ion by direct summation, with emission of anti-Stokes radiation. Up to the present, most of the experimental examples of anti-Stokes fluorescence involved principally the rare earth ions (1). Several mechanisms are proposed to explain these phenomena: the summation of infrared photons is produced by means of cooperative processes or successive absorption with or without energy transfers; the transfer between pair ions being resonant or phonon assisted.

We found that tetravalent uranium as a doping ion in thorium tetrahalides acts as an up converter in single-crystal as well as

in polycrystalline powder. Recently, we have shown (2) that in the case of  $ThBr_4$  and  $ThCl_4$  doped with a low concentration of tetravalent uranium (a few hundred of ppm) infrared excitation with  $\lambda > 0.82 \mu m$  at room temperature produces a bright emission in the red region. At lower temperature (near the phase transition temperature, 100 K) a weak green fluorescence appears.

In this paper, we report on an investigation of the up conversion process of  $U^{4+}$  doped  $ThBr_4$ . Besides sample geometry consideration, the mechanism has been determined and the absolute conversion efficiency measured. Some comparative results will be reported for  $ThCl_4$ .

### Experimental Details

The single crystals of  $ThBr_4$  (and  $ThCl_4$ ) doped with different concentration of uranium were grown by the Bridgman method previously described (3). The uranium concentration in the matrix was determined by

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counting the alpha decay of the isotopes  $^{238}U$  and  $^{235}U$  after a chemical separation on anionic resin of  $Th^{4+}$  from  $U^{4+}$  (4). Experiments were done on single crystals and on microcrystalline powder with different calibrated grain sizes (0.068, 0.132, 0.258, 0.53, and 1 mm) and with different dopant concentrations (0.006, 0.024, 0.050, and 0.25 at.%  $U^{4+}$  in  $ThBr_4$ ). Since the crystals are hygroscopic, samples were handled under an inert atmosphere, and transferred to a silica tube sealed under vacuum.

Difficulties of reproducibility in the relative intensity measurements were due to the heating of the samples by the infrared radiation. Thermal quenching had been avoided by using a Peltier effect cooling system. Through this device, the temperature of the sample is maintained almost constant.

Relative intensity and spectral measurements of the red fluorescence at  $0.695 \mu m$  for  $ThBr_4$  and  $0.689 \mu m$  for  $ThCl_4$  were obtained with a Jobin Yvon HR1000 monochromator: the excitation source was a 1-kW tungsten iodine lamp. All visible stray light was stopped by two filters ORIEL J820a and DJ845. Visible light emitted by the samples was detected by a photomultiplier Hamamatsu R376.

The double-beam excitation spectra using the setup described Fig. 1 were obtained

with the monochromator centered at  $0.695 \mu m$  for  $ThBr_4$  and  $0.689 \mu m$  for  $ThCl_4$ . The sample is excited both by a continuous infrared broadband beam ( $0.82\text{--}2 \mu m$ ) and by a monochromatic beam through an ORIEL monochromator model 7240, in the range 0.8 up to  $1.2 \mu m$  (with  $\Delta\lambda = 0.01 \mu m$ ) produced by the same 1-kW tungsten iodine lamp.

The absolute conversion efficiency at visible wavelength of the sample was measured using a high-efficiency GaAs:Si diode (Plessey, GAL10) emitting 45 mW at  $\approx 0.96 \mu m$ .

Lifetime measurements were obtained through a Lecroy 3500 M multichannel analyzer system in the 500-ns to 100- $\mu s$  range using a Lecroy M2256 transient digitizer.

## Experimental Results

### Up Conversion Process of $U^{4+}$ : $ThBr_4$

When exciting  $U^{4+}$  in  $ThBr_4$  with infrared ( $\lambda > 0.82 \mu m$ ) at room temperature, we observed an anti-Stokes fluorescence in the red between  $0.67$  and  $0.72 \mu m$  (2), corresponding to a  $^3P_0 \rightarrow ^3H_4$  transition (5). The number of photons involved in this process is determined from measurements of the up converted light intensity as a function of the exciting power  $I_u = f(W^n)$ . Figure 2 shows the power law of the red emission in its

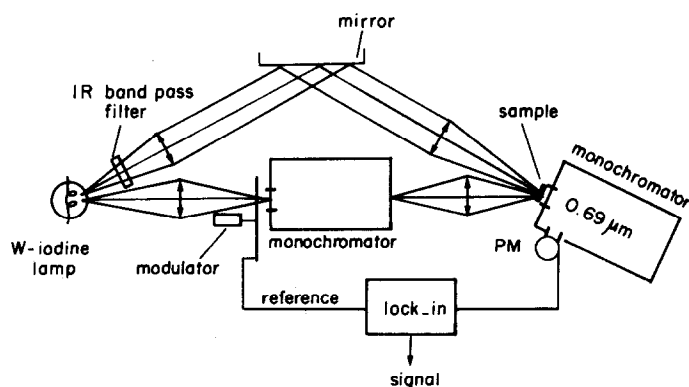


FIG. 1. Double-beam excitation experimental setup.

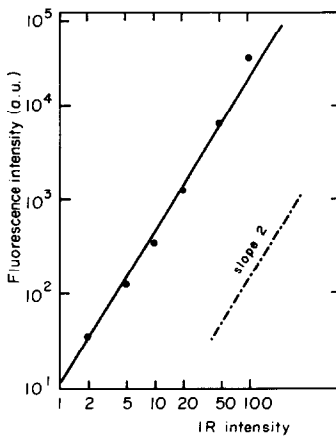


FIG. 2. Variation of the fluorescence intensity with the intensity of the IR excitation.

dependence on the infrared excitation. On crystals as well as on microcrystalline calibrated powder, the power law is found to be quadratic with respect to the infrared excitation (2). This is evidence which shows that excitation involves a two-photon process. Furthermore, we studied the variation of the red fluorescence intensity with the concentration of the tetravalent uranium. We found that the  $0.695\text{-}\mu\text{m}$  emission follows a linear law with  $\text{U}^{4+}$  concentration as shown in Fig. 3 for a concentration ranging from 0.006 to 0.05%. From this result we can conclude that the absorption of two infrared photons occurs through one  $\text{U}^{4+}$  ion

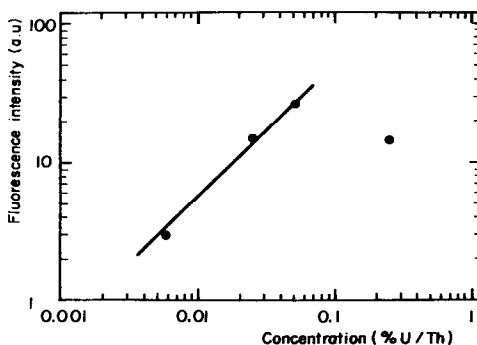


FIG. 3. Variation of the fluorescence intensity at  $0.69\text{ }\mu\text{m}$  with  $\text{U}^{4+}$  concentration.

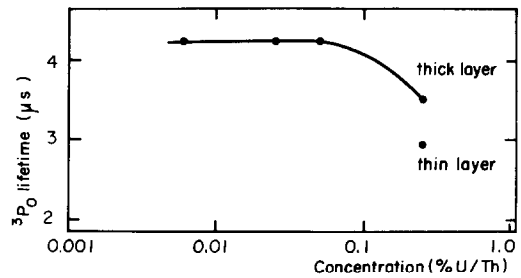


FIG. 4.  ${}^3\text{P}_0$  radiative lifetime behavior versus concentration for  $\text{U}^{4+}:\text{ThBr}_4$ .

in reaching the  ${}^3\text{P}_0$  excited state, which, by spontaneous decay, gives rise to a visible fluorescence. For higher concentrations, beyond 0.05%, the decrease of the conversion efficiency as well as the decrease of lifetimes shown in Figs. 3 and 4 indicate a quenching effect.

#### Compared Characteristic Samples

Red fluorescence intensity measurements have been performed on single crystals with different thickness as well as on powder with different grain size for  $\text{U}^{4+}$  concentration of 0.006, 0.025, 0.05, and 0.25%, during which the conditions of excitation, geometry, and temperature were held fixed. Results obtained for both single crystals and powder are represented in Figs. 5a,b. Emission intensities at  $0.695\text{ }\mu\text{m}$  are given in arbitrary units. At each concentration, the variation in fluorescence intensity versus thickness of the single crystals and grain size of the powder is similar: an optimum is found at higher concentration due to reabsorption, as shown by the flatness of curves at lower concentrations (Fig. 5a). Conversion efficiency is found to be optimized for single crystals at a thickness of about 0.9 mm and at a concentration of 0.05%; for microcrystalline powder, at a grain size of approximately 0.2–0.3 mm, and at the same concentration as for single crystals. In that case the efficiency is multiplied by a factor of 20 in comparison with the same single-crystal sample. This is be-

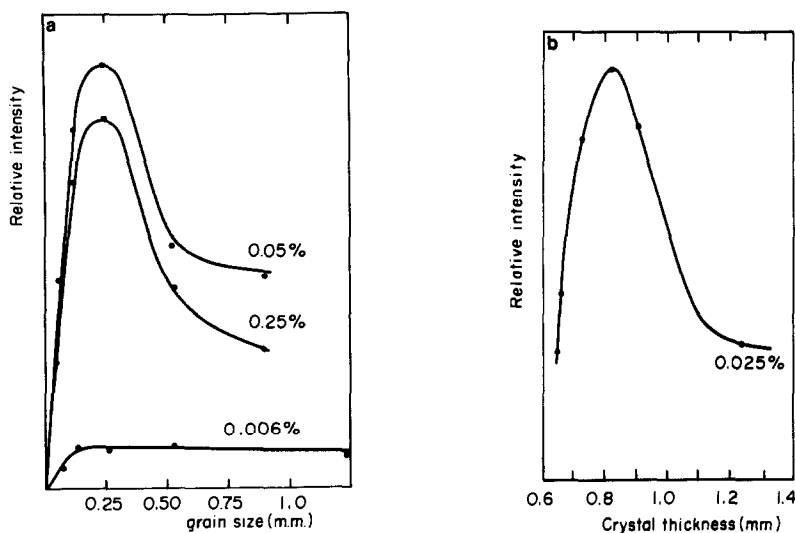


FIG. 5. (a) Emission intensity versus grain size of  $ThBr_4$  powder with 0.05, 0.25, and 0.006% of  $U^{4+}/Th^{4+}$ . (b) Emission intensity versus thickness of  $U^{4+}:ThBr_4$  single crystals with 0.025% of  $U^{4+}/Th^{4+}$ .

lied to be due to photon trapping, as demonstrated by lifetime measurements versus sample shapes (6) (Fig. 4). As a matter of fact, the  $^3P_0$  lifetime of  $\tau = 3,50 \mu s \pm 0,05$  for thick single crystals (with 0.25% of  $U^{4+}$ ) becomes  $2.95 \mu s \pm 0.05$  on a thin single crystal. The measured increase of lifetime with sample size is evidence for radiation trapping arising from radiative transfer.

#### Excitation Spectra Experiments

For excitation spectra, the double-beam technique already described (7) has been used to determine the energy of the protons producing the red fluorescence.

The double-beam excitation spectra for emission at  $0.695 \mu m$  (Fig. 6) shows that  $^3P_0$  excitation is obtained by absorption of photons at  $0.95$  and  $1.17 \mu m$ .

Comparing excitation spectra with room-temperature absorption spectra as shown in Fig. 7, indicates that the anti-Stokes fluorescence derived from the upper  $^3P_0$  level is induced from the summation of photons corresponding to the  $^3H_4 \rightarrow ^3H_6$  ( $0.95 \mu m$ ) or  $^3H_4 \rightarrow ^3F_3$  ( $1.17 \mu m$ ) transitions. The fact

that an emitting IR diode alone centered at  $0.96 \mu m$  induces a red fluorescence  $^3P_0 \rightarrow ^3H_4$  shows that this excitation is obtained through absorption by  $U^{4+}$  of photons at  $0.95 \mu m$  in a  $^3H_4 \rightarrow ^3H_6$  transition; then the same  $U^{4+}$  ion absorbs a second photon at  $0.95 \mu m$  which is added, after multiphonon relaxation, to the first to reach the  $^3P_0$  level.

In summary, we can conclude that the  $^3P_0$  red emission at  $0.695 \mu m$  is excited by  $0.95$ -plus  $1.17$ - $\mu m$  photons, as well as by absorption of two  $0.95$ - $\mu m$  photons or of two  $1.17$ - $\mu m$  photons as shown in Figs. 8a-f.

In the same manner, the double-beam excitation spectra have been obtained for  $U^{4+}$ :

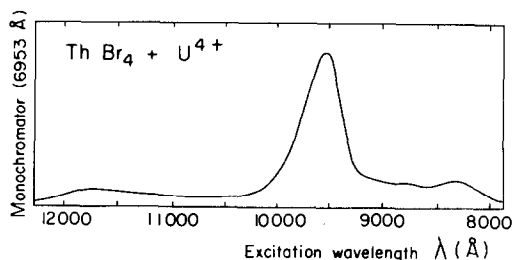


FIG. 6. Double-beam excitation spectrum for  $U^{4+}:ThBr_4$  at  $0.695 \mu m$ .

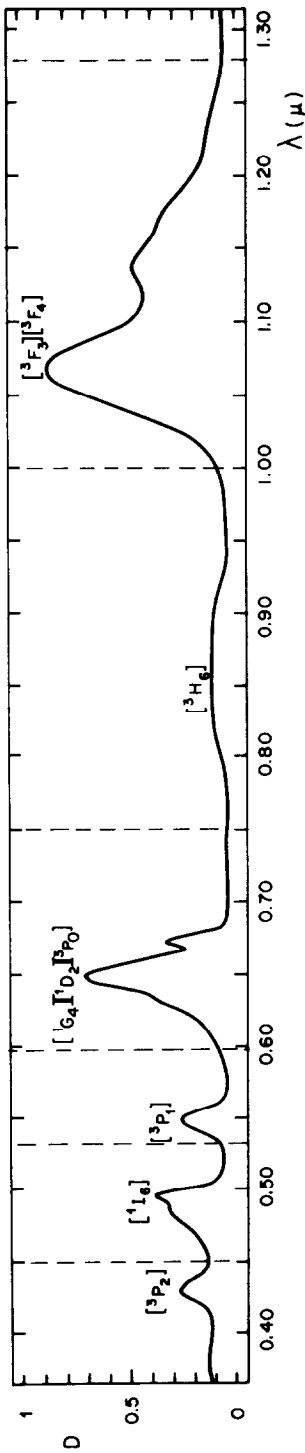


FIG. 7. Absorption spectrum of  $U^{4+}$ :  $ThBr_4$  at room temperature.

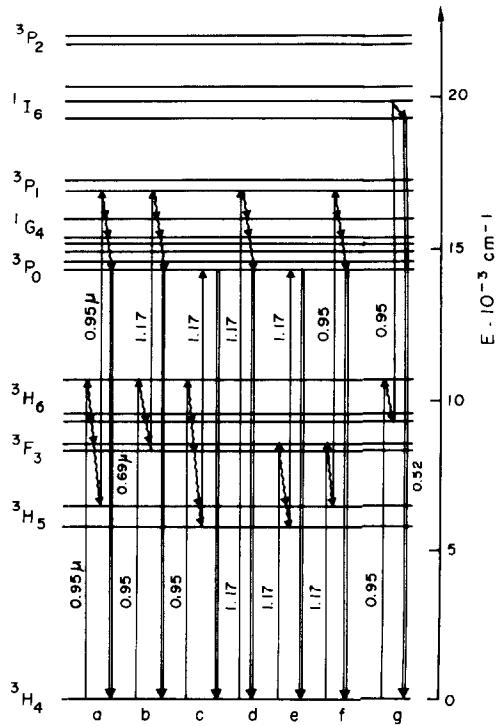


FIG. 8. Different excitation routes for the IR excited red emission (a-f) and for the green emission process (g).

$ThCl_4$  using a monochromator centered at  $0.689 \mu m$ . The spectrum reported in Fig. 9 shows that the red emission from  $^3P_0$  is mainly obtained by the absorption of photons at  $0.94, 0.931,$  and  $0.989 \mu m$ , corresponding to the  $^3H_4 \rightarrow ^3H_6$  transitions.

For this sample we verified that an emit-

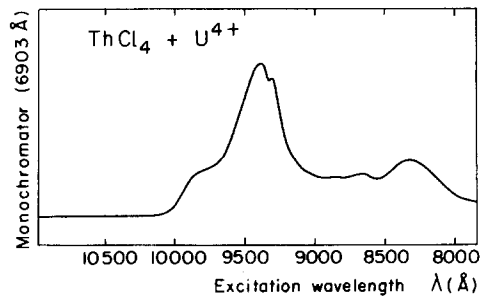


FIG. 9. Double-beam excitation spectrum for  $U^{4+}$ :  $ThCl_4$  at  $0.689 \mu m$ .

ting IR GAL 10 diode centered at 0.96  $\mu\text{m}$  also induced the red fluorescence at 0.689  $\mu\text{m}$ .

### Discussion

The  $^3\text{H}_6$  state which is excited by a 0.95- $\mu\text{m}$  photon relaxes toward  $^3\text{H}_5$  by multiphonon de-excitation; then  $^3\text{H}_5$  is excited by a second 0.95- or 1.17- $\mu\text{m}$  photon to reach the  $^3\text{P}_0$  state after multiphonon relaxation, or directly. A direct summation of two 1.17- $\mu\text{m}$  photons or of one 1.17- plus one 0.95- $\mu\text{m}$  photon, with phonon assisted de-excitation through the  $^3\text{F}_3$  state also leads to  $^3\text{P}_0$ . However, it seems from the normalized double-beam spectra (Fig. 6) that the summation of two 0.95- $\mu\text{m}$  photons could be more efficient than the summation of two different energy photons or of two 1.17- $\mu\text{m}$  photons.

Taking into account excitation cross section  $\sigma_1$  and  $\sigma_2$ , respectively, from level 1 ( $^3\text{H}_4$ ) to level 2 ( $^3\text{H}_{6,5}$  and  $^3\text{F}_{3,4}$ ) and from level 2 to level 3 ( $^3\text{P}_0$ ,  $^1\text{G}_4$ ,  $^3\text{P}_1$ ), the population variation of levels 2 ( $^3\text{H}_{6,5}$  and  $^3\text{F}_{3,4}$ ) and levels 3 ( $^3\text{P}_0$ ,  $^1\text{G}_4$ ,  $^3\text{P}_1$ ) are given by the following equations:

$$\frac{dn_2}{dt} = \sigma_1\phi_1n_1 - n_2/\tau_2 - \sigma_2\phi_2n_2 + n_3/\tau_3$$

$$\frac{dn_3}{dt} = \sigma_2\phi_2n_2 - n_3/\tau_3$$

where  $\phi_i$  represents the infrared incident flux, and  $\tau_i$ , the lifetime of the  $i$ th level, and where levels connected by nonradiative transitions have been lumped together as levels 2 and 3.

For steady state conditions, the above reduces to

$$n_3 = \phi_1\phi_2\sigma_1\sigma_2n_1\tau_2\tau_3 \quad (1)$$

which, in the case of equal energy photon excitation, yields

$$n_3 = \phi^2\sigma_1\sigma_2n_1\tau_2\tau_3.$$

This formula well describes the linear variation with concentration and the quadratic one with excitation flux. Further the absorption oscillator strength at 0.95  $\mu\text{m}$  for the  $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transition and 1.17  $\mu\text{m}$  for the  $^3\text{H}_4 \rightarrow ^3\text{F}_3$  transition have been already measured (4) as  $1.05 \times 10^{-4}$  and  $2.8 \times 10^{-4}$ , respectively. These large values, roughly  $10^2$  times larger than for rare-earth ions explain the fact that sequential absorption is encountered here and that concentration quenching occurs at concentrations as low as 0.25%. Along this line it can be noted that red fluorescence is also observable in a pure ThBr<sub>4</sub> crystal containing uranium as unwanted impurity (a few ppm). Moreover, the  $^3\text{H}_4 \rightarrow ^3\text{P}_0$  oscillator strength ( $0.8 \times 10^{-4}$ ) permits calculation of the radiative lifetime. At room temperature, the  $^3\text{H}_4$  ground state has a large splitting (5) (0, 109, 148, 657, 707, 864, and 980  $\text{cm}^{-1}$ ). Taking into account an effective degeneracy of approximately 4 due to the large splitting, we calculated a radiative lifetime approximately  $\tau_0 \approx 6.1 \mu\text{s}$  for the  $^3\text{P}_0$  state. Direct measurement on the  $^3\text{P}_0$  transition yields  $\tau_{\text{meas}} = 4.5 \mu\text{s}$ , and a quantum efficiency for  $^3\text{P}_0$  of  $\eta \approx 0.74$ . Also, quantum efficiency of  $^3\text{H}_5$  can be estimated to be larger than  $\eta$  since the energy gap below  $^3\text{H}_5$  is larger than the one below  $^3\text{P}_0$ . The increase in up conversion intensity with photon trapping is directly related to lifetime increases in Eq. (1). These facts jointly explain why sequential absorption is easily observed in  $\text{U}^{4+}:\text{ThBr}_4$ .

The standardized conversion efficiency at visible wavelength is the ratio of the emitted light intensity to the absorbed infrared radiation intensity, multiplied by the  $n$ th power of the excitation level  $P_{\text{ex}}$ ,  $n$  being the number of photons involved in the up conversion process (8).

$$\eta_n = \frac{P_{\text{em}}}{(P_{\text{ex}})^{n-1} (\text{absorbed IR power})} \quad (\text{W/cm}^2)^{-(n-1)}.$$

The absolute measurements of conversion efficiency have been performed on microcrystalline powder with grain sizes of about 0.2–0.3 mm and a concentration of 0.05%, which is directly irradiated by an emitting IR diode GAL 10 (PLEYSSEY) centered at 0.96  $\mu\text{m}$ . Through a photomultiplier of known spectral sensitivity an excitation level of 2 mW yields a standardized conversion efficiency  $\eta_n = 2 \times 10^{-6} \text{ cm}^2/\text{W}$ . Taking into account that the 1.17- $\mu\text{m}$  photon is also efficient in inducing the red fluorescence, the absolute conversion efficiency could be larger for broadband excitation.

Whatever the excitation, UV or IR, the intensity of the visible emitting light increases with decreasing temperature. At 4.2 K, the infrared excited fluorescence intensity is enhanced by a factor 50 in comparison with that measured at room temperature. Furthermore, an extra green emission which is very weak (about 200 times less than the red emission) is observed below 100 K at about 0.52  $\mu\text{m}$  and is derived from the  $^1\text{I}_6$  state. The up conversion fluorescence spectrum at 4.2 K is shown in Fig. 10. Other extra weak lines are observed. The increase of the visible emitted light with decreasing temperature makes the green emission observable. From Fig. 8 route g shows that the summation of two 0.95- $\mu\text{m}$  photons permits to the  $^1\text{I}_6$  state to be reached; after phonon relaxa-

tion it fluoresces toward  $^3\text{H}_4$ . The mechanism for this green fluorescence has not yet been studied and a possible connection with the incommensurate phase transition below 95 K (5–9, 10) has not yet been investigated.

Concerning the up conversion mechanism in  $\text{U}^{4+}:\text{ThCl}_4$  the fluorescence intensity variation with the  $\text{U}^{4+}$  concentration and with the infrared radiation intensity has not been studied. We can suppose that it is about the same as in  $\text{U}^{4+}:\text{ThBr}_4$  since these crystals are isomorphous. In both cases  $\text{U}^{4+}:\text{ThBr}_4$ ,  $\text{ThCl}_4$  the red fluorescence corresponds to the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transitions and photons at 0.95  $\mu\text{m}$  for  $\text{ThBr}_4$  and 0.94  $\mu\text{m}$  for  $\text{ThCl}_4$  corresponding to  $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transition induce the anti-Stokes fluorescence. However, for  $\text{U}^{4+}:\text{ThCl}_4$  it seems that only two equal energy photons are principally responsible for the red fluorescence.

The same phenomenon has been observed with  $\text{Np}^{4+}(5f^3)$  in the two matrices  $\text{ThBr}_4$  and  $\text{ThCl}_4$ , which leads us to think that the up conversion process well known in the 4f ions could play a similar role in the 5f elements, with an enhanced effect due to higher oscillator strengths.

## References

1. F. AUZEL, *Proc. IEEE* **61**, 758 (1973).
2. M. GENET, S. HUBERT, AND F. AUZEL, *C.R. Acad. Sci. Paris* **293**, 267 (1981).

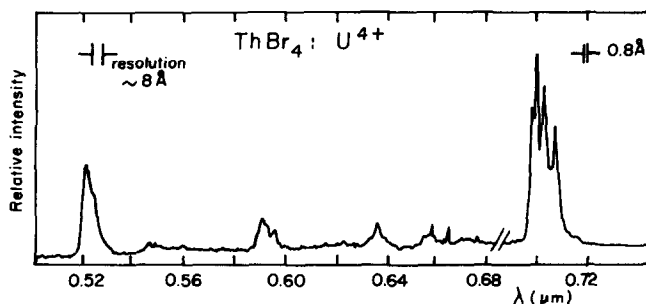


FIG. 10. IR excited fluorescence spectrum of  $\text{U}^{4+}:\text{ThBr}_4$  at 4.2 K.

3. M. HUSSONNOIS, J. C. KRUPA, M. GENET, L. BRILLARD, AND R. CARLIER, *J. Crystal Growth* **51**, 11 (1981).
4. F. AUZEL, S. HUBERT, AND P. DELAMOYE, *J. Luminescence* **26**, 251 (1982).
5. P. DELAMOYE, K. RAJNAK, M. GENET, AND N. EDELSTEIN, *Phys. Rev.* **28**, 4923 (1983).
6. F. AUZEL AND D. PECILE, *C.R. Acad. Sci. Paris* **277**, 155 (1973).
7. F. AUZEL, *C.R. Acad. Sci. Paris* **263**, 819 (1966).
8. F. AUZEL AND D. PECILE, *J. Luminescence* **11**, 321 (1976).
9. S. HUBERT, P. DELAMOYE, S. LEFRANT, M. LEPOSTELLEC, AND M. HUSSONNOIS, *J. Solid State Chem.* **36**, 36 (1981).
10. L. BERNARD, R. CURRAT, P. DELAMOYE, C. M. E. ZEYEN, S. HUBERT, AND R. DE KOUCHKOVSKY, *J. Phys. C* **16**, 433 (1983).