

Strong and weak up-conversion rate in $\text{LaCl}_3: \text{U}^{3+}$ single crystal

P.J. Deren^{a,*}, R. Mahiou^b, J.C. Krupa^c

^a Instytut Niskich Temperatur i Badań Strukturalnych PAN im W. Trzebiatowskiego, ul. Okolna 2, Skr. Pocz. 1410, 50950 Wrocław 2, Poland

^b Laboratoires des Matériaux Inorganiques, UMR 6002-CNRS, Université Blaise Pascal, et ENSCCF, F-63177 Aubiere Cedex, France

^c Institute de Physique Nucleaire, CNRS, IN2 P3, 91406 Orsay Cedex, France

Abstract

Up-conversion in $\text{LaCl}_3: \text{U}^{3+}$ single crystal was observed. It was found that up-conversion mechanism depends on excitation mode; pulse excitation leads to cross-relaxation up-conversion, for the case of continuous excitation excited state absorption dominates in the LaCl_3 crystal. © 2004 Elsevier B.V. All rights reserved.

Keywords: LaCl_3 single crystal; U^{3+} ions; Up-conversion mechanism

1. Introduction

Emission of higher energetic photons than excitation's photons has been investigated widely since many years in crystals and glasses doped with rare-earth ions and transition metal elements. This phenomenon sometimes is very useful to obtain anti-Stokes emission, sometimes is less favourable when efficiently depopulates emitting level [1]. In practical applications two up-conversion mechanisms are considerable: energy transfer up-conversion (ETU) and excited state absorption (ESA). ETU proceeds in a pair of ions; ESA is a one-ion process. The energy conservation principle could not be broken, therefore, both processes requires a least two low energetic photons to achieve upper level. The number of photons involved in the process is derived usually from an allometric function:

$$I_{\text{em}} = I_{\text{ex}}^n \quad (1)$$

where I_{em} is intensity of the emission, I_{ex} intensity of the excitation and n understand as number of photons involved in the process. Pollnau et al. [2] discussed recently intensity of up-conversion in function of excitation power.

The up-conversion in $\text{LaCl}_3: \text{U}^{3+}$ were already investigated [3–10]. In this work, we present the results of experiments of pulse and continuous up-conversion in LaCl_3 single crystal doped with U^{3+} ions. The crystal was excited in the IR region at about $1 \mu\text{m}$. Two limits were observed of

high and low up-conversion rate depending on work regime of the excitation source.

2. Experimental

The LaCl_3 crystal was grown by the Bridgman method, the concentration of uranium ions was 1 wt.%. The sample was cleaved to rectangular form with size ($15 \text{ mm} \times 3 \text{ mm} \times 3 \text{ mm}$) and closed in a quartz ampoule filled with He gas.

The emission spectra were recorded on a TH 1000 monochromator equipped with an R928 Hamamtsu photomultiplier. A Continuum Surelite I pulse dye laser pumped by a Continuum ND60 Nd:YAG (9 ns pulse width) laser was used for excitation. A homemade Raman H_2 cell was used to enhance the tuning range of the dye laser. Continuous excitation was performed with a Spectra Physics Ti-Sapphire laser pumped by an argon laser. The sample was cooled down in a helium cryostat. All experiments were done at 10 K. Both excitations, pulse and continuous was focused on the sample with an 8 cm lens.

Decay profiles were recorded on a Lecroy digital oscilloscope. Time resolved spectra were collected in a Boxcar Averager Model 162 by Princeton Applied Research. A PC drove the whole system.

3. Results

Pulse as well as continuous wave (cw) excitation at about $1 \mu\text{m}$ produces strong emission in the visible (see Fig. 1).

* Corresponding author.

E-mail address: deren@int.pan.wroc.pl (P.J. Deren).

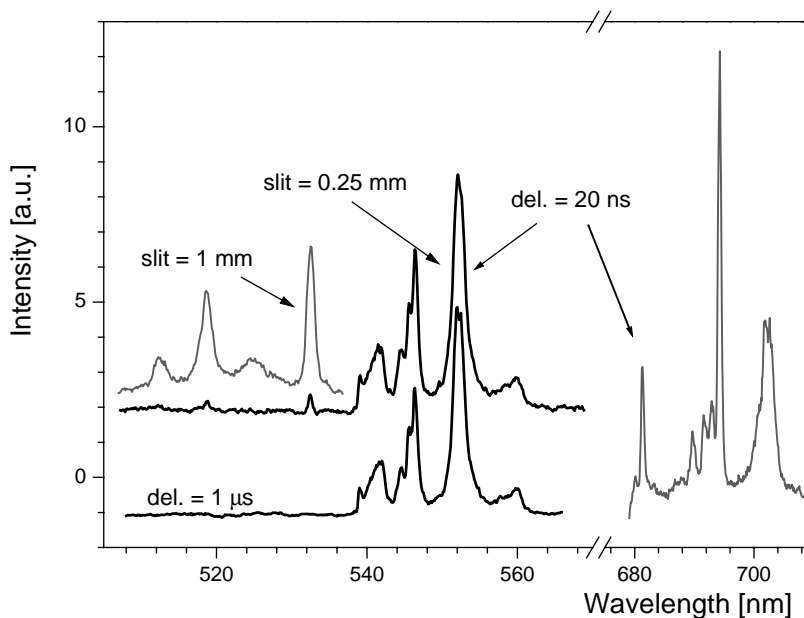


Fig. 1. Time resolved up-conversion emission of $\text{LaCl}_3: \text{U}^{3+}$ at 16 K, $\lambda_{\text{exc}} = 978.39 \text{ nm}$.

Three narrow lines in the excitation spectrum labelled *a*, *b*, *c* (see Fig. 2) do not correspond to the U^{3+} absorption spectrum from the ground level. They were attributed to the absorption from the excited states and two-photon absorption within U^{3+} [10]. The up-conversion emission intensity in function of excitation power had almost quadratic dependence indicating on two-photon process [2].

Excitation by a pulse laser at about $1 \mu\text{m}$ produces also strong visible emission of the $\text{LaCl}_3: \text{U}^{3+}$, but contrary to the previous one the pulse excitation spectrum is broad and has a maximum at 978.3 nm , no characteristic narrow

three lines are observed (see Fig. 2). When excitation was tuned to higher energies, the up-conversion emission becomes stronger and reaches its maximum for the 1002.2 nm excitation (see Fig. 3).

Integrated up-conversion emission intensity versus excitation power, contrary to the cw excitation has almost linear dependence.

Emission decay profiles were very helpful to explain the mechanism of pulse up-conversion emission. They are different for Stokes and anti-Stokes emission (see Fig. 4). First of all the green Stokes emission decays very fast, its decay

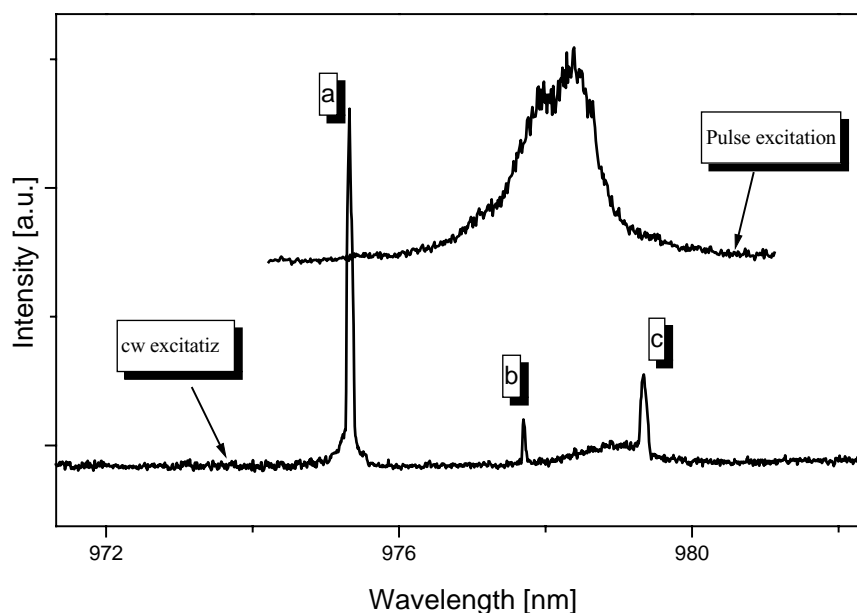


Fig. 2. Excitation spectra of anti-Stokes emission of $\text{LaCl}_3: \text{U}^{3+}$, $T = 10 \text{ K}$, upper curve-pulse excitation, lower curve continuous excitation.

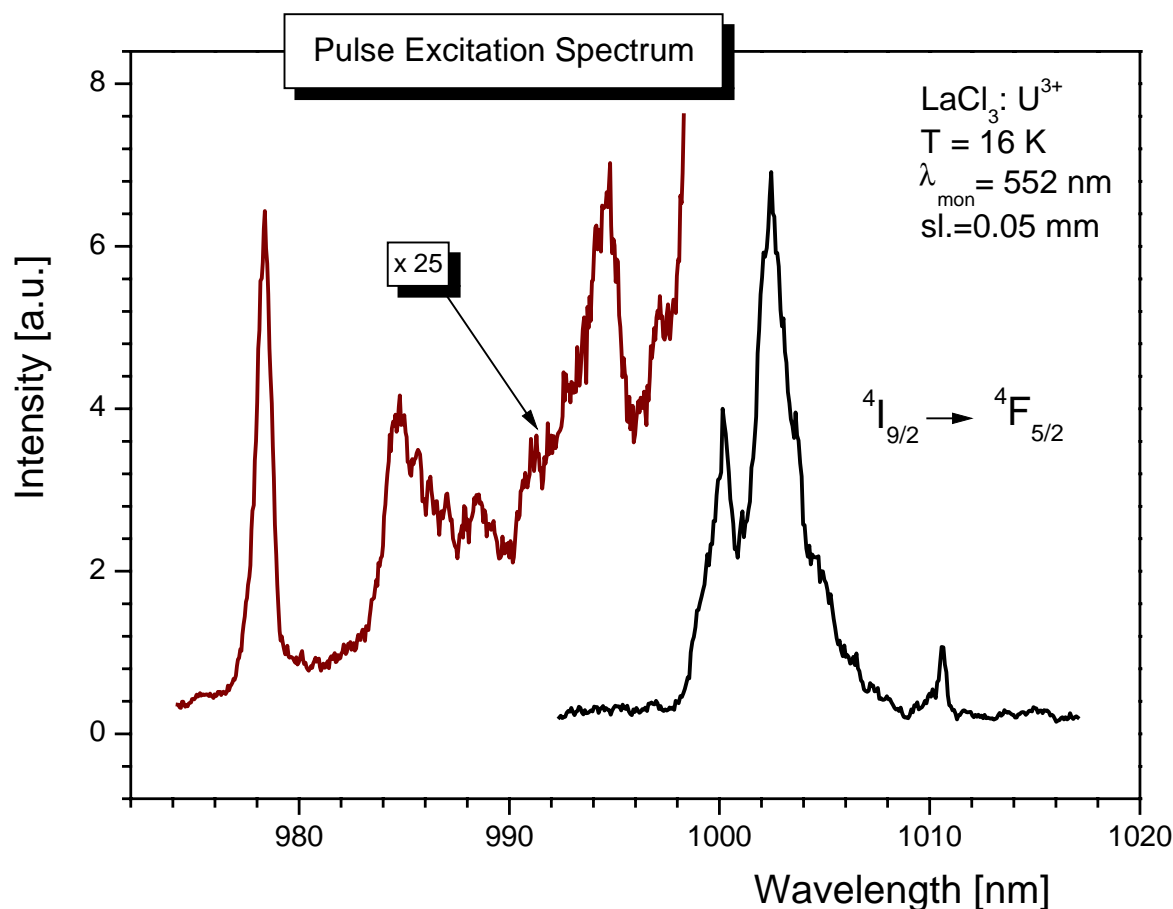


Fig. 3. Pulse excitation spectra of $\text{LaCl}_3: \text{U}^{3+}$, $T = 10 \text{ K}$.

time was only 100 ns. However the up-conversion emission appears just after the excitation pulse and at the beginning decays fast (100 ns), it lasts much longer. Decay constant of second component was equal to $3.8 \mu\text{s}$. The red anti-Stokes emission has relatively long— $3 \mu\text{s}$ rise time, time constant is equal $14 \mu\text{s}$.

In the green region, the emission, however, is observed not only from the ${}^2\text{K}_{15/2}$ term, but also from the upper ${}^2\text{H}_{11/2}$ level (see Fig. 2). The up-conversion emission from this level is characterised by short decay time, exactly the same as Stokes one, it disappears after $1 \mu\text{s}$ (see Fig. 1).

4. Discussion

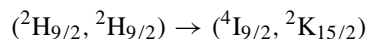
Following the energy level assignment reported by Carnall [11] line *a*, *b* and *c* correspond to ESA [10]. Possible mechanisms are shown in Fig. 5. The line *a* corresponds to the ${}^2\text{H}_{9/2} \rightarrow {}^2\text{H}_{11/2}$ transition.

The line *b* is only involved in the red emission and was attributed to the following resonant process: ${}^4\text{I}_{11/2} \rightarrow {}^4\text{F}_{9/2}$. The line *c* is due to two-photon absorption: ${}^4\text{I}_{9/2} \rightarrow {}^2\text{D}_{5/2}$.

The results collected in Section 3 show that the up-conversion emission is excited by different mechanisms

depending on excitation regime, i.e. cw or pulse. The excitation spectra are different, for cw—excitation narrow lines are observed, which origin is due to ESA, for the pulse excitation instead of three lines one, broad line is observed. Pulse excitation spectrum recorded for broader range shows lines due to absorption from the ${}^4\text{I}_{9/2}$ ground level to the ${}^4\text{F}_{5/2}$ one at 9975 cm^{-1} (1002.2 nm) (see Fig. 3). Line at 10254 cm^{-1} (975.2 nm) is due to vibronic component of the ${}^4\text{F}_{5/2}$ level; it is 20 times weaker than main electronic one.

The green up-conversion emission decays longer than Stokes one indicating on energy transfer in a cross-relaxation up-conversion. This resonant process is described as follows (see Fig. 6):



$$9444, 9444 \rightarrow 208, 18\,680 + 416 (\text{cm}^{-1})$$

and could be described by following equation set:

$$\begin{aligned} \frac{dn_2}{dt} &= -k_2n_2 - 2k_{\text{CR}}n_2^2, \\ \frac{dn_3}{dt} &= -k_3n_3 + k_{\text{CR}}n_2^2, \end{aligned} \quad (2)$$

where n_i and k_i are population and transfer rate, respectively, of level “*i*”, k_{CR} is cross-relaxation transfer rate. The ${}^2\text{H}_{9/2}$

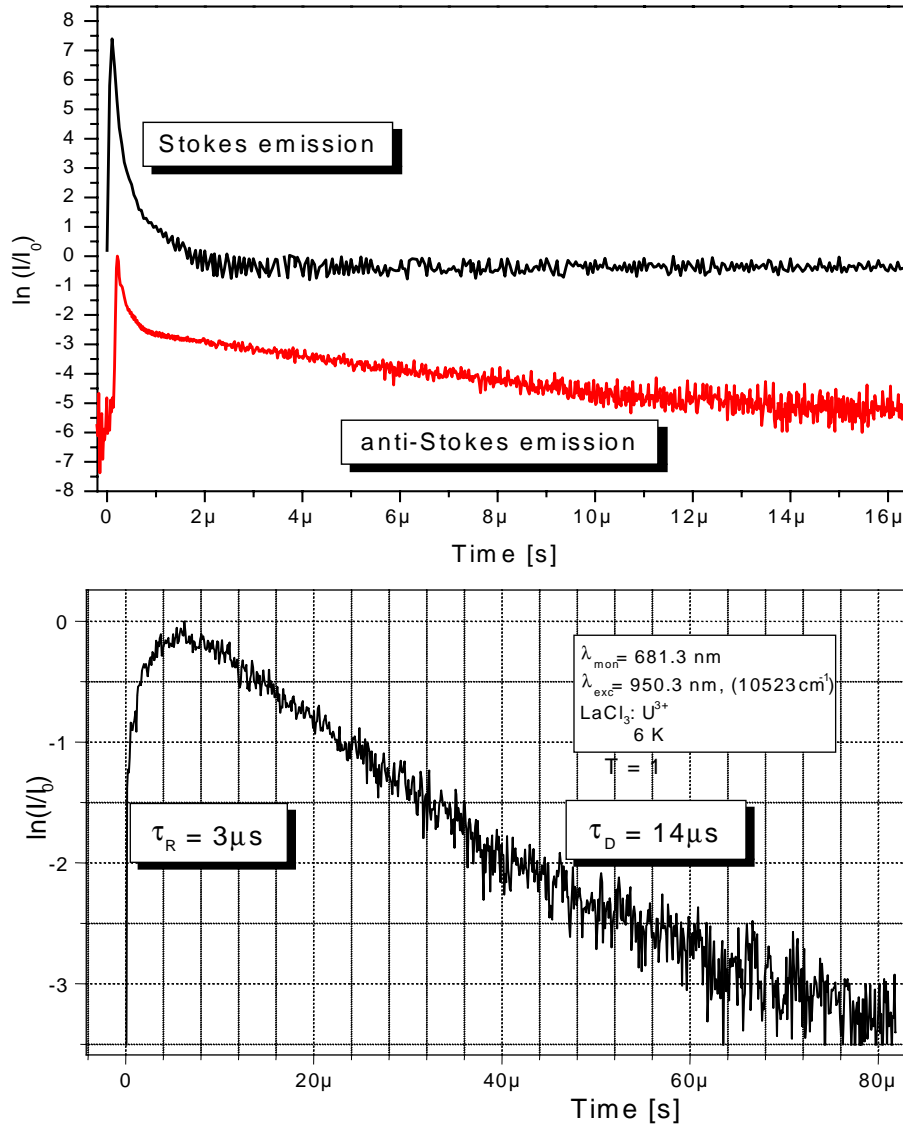


Fig. 4. Decay profiles of Stokes and anti-Stokes emissions of $\text{LaCl}_3: \text{U}^{3+}$, $T = 10 \text{ K}$.

level is populated via nonradiative transition from the $^4\text{F}_{5/2}$ one.

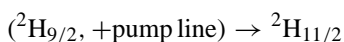
First of the equation set has solution after supposition, that $n_2(0) = N$ and k_{CR} is small and than negligible:

$$n_2(t) = Ne^{-k_2t} \quad (3)$$

Putting this into second equation and after supposition $n_3(0) = 0$ it is possible to obtain population of the level 3:

$$n_3(t) = -\frac{N^2 k_{\text{CR}}}{2k_2 - k_3} (e^{-2k_2t} - e^{-k_3t}) \quad (4)$$

One can see that decay time of the up-conversion emission from the $^2\text{K}_{15/2}$ term (level 3) is equal half of the $^2\text{H}_{9/2}$ decay time (level 2) and has rise time $1/k_3$. This rise time is not observed because is hidden in an ESA process (see Fig. 6):



$9444, 10254 \rightarrow 19698 + 39 \text{ (cm}^{-1}\text{)}$.

The question arises, why the slope is different for the same emission depending on the excitation regime? Pollnau et al. [2] showed that only in the case of weak up-conversion rate (ESA or cross-relaxation) the slope of the up-conversion emission intensity versus excitation power is equal with the number of photons involved in the process and it is observed in the cw excitation experiment. In the pulse experiment, the cross-relaxation up-conversion is much more efficient than nonradiative transitions to the lower levels, therefore the “slope” was close to 1. When pump power increases competition between up-conversion and linear decay and consequently slope of the emission versus excitation power decreases.

In our experiment, we changed only the regime of the excitation from continuous to pulse. In both cases, we preserved the same conditions, like: temperature, polarisation

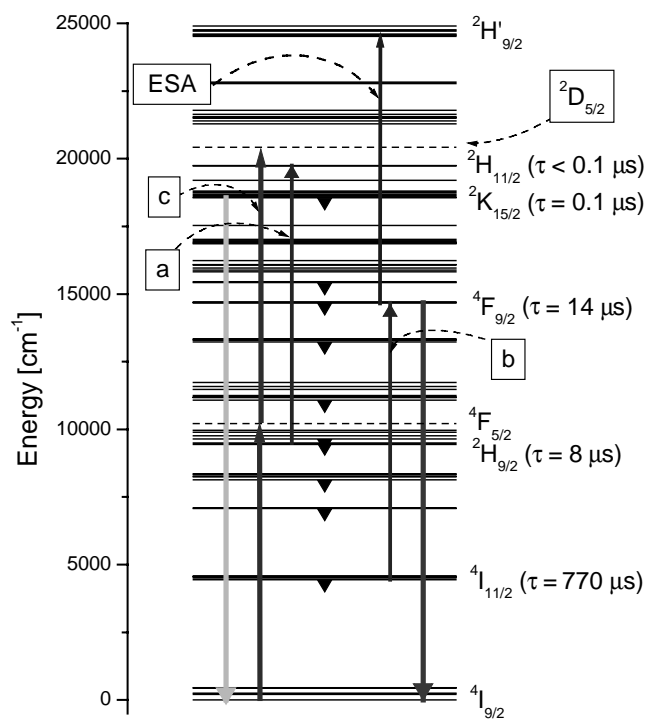


Fig. 5. Possible mechanisms of up-conversion emission excited by continuous excitation.

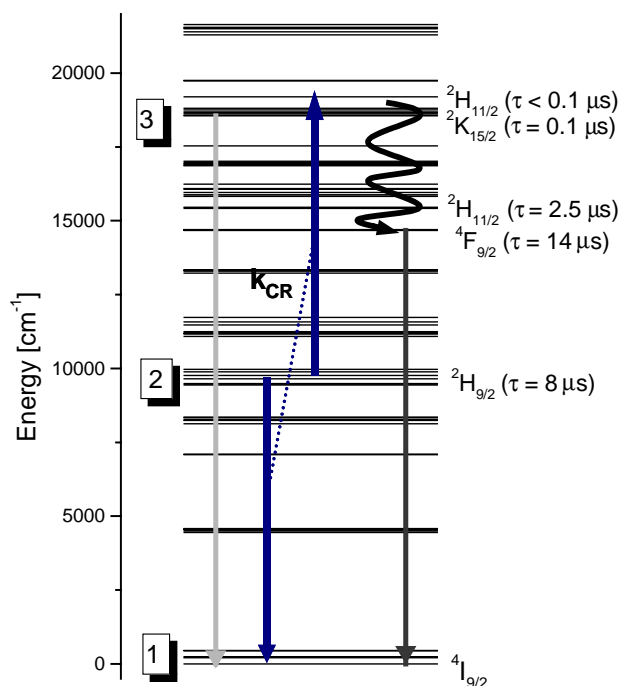


Fig. 6. Possible mechanisms of up-conversion emission excited by pulse excitation.

and wavelength of the excitation. In both experiments, the excitation was focused on the sample by the same manner. Excitation power was 7–200 mW for cw excitation, for the pulse excitation the energy of the pulse was from 7 μ J to 40 mJ, it gives for the 7 ns pulse range from 10 up to 570 kW per pulse.

5. Conclusions

It was shown, on $\text{LaCl}_3: \text{U}^{3+}$ example, that nature of the excitation imposes the nature of the up-conversion. Continuous wave excitation leads to excited state absorption, while pulse excitation provokes cross-relaxation up-conversion. The cross-relaxation up-conversion is not observed in the case of cw excitation, if it would had been present the excitation spectra would have been the same in both cases. The cw excitation spectrum is due to transition between the excited levels. On the other hand, for the pulse excitation the excitation spectrum is due to transition from the ground level.

The ESA is one ion process, cross-relaxation up-conversion occurs in a pair of ions. Therefore, we may conclude that cooperative processes are better observed in the case of pulse excitation. For the continuous excitation one ion ESA process dominates in the LaCl_3 crystal.

Acknowledgements

This work was performed within the frame of a mutual French–Polish (CNRS–KBN) scientific cooperation programme—PICS.

References

- [1] F. Auzel, in: B. di Bartolo (Ed.), *Nonlinear Spectroscopy of Solids, Advanced and Applications*, Plenum Press, New York, 1994.
- [2] M. Pollnau, D.R. Gamelin, S.R. Luthi, H-U. Güdel, M.P. Hehlen, *Phys. Rev. B* 61 (5) (2000) 3337.
- [3] P.J. Deren, J. Feries, J.-C. Krupa, W. Strek, *Chem. Phys. Lett.* 264 (6) (1997) 614.
- [4] P.J. Deren, J.-C. Krupa, W. Strek, *J. Lumin.* 72–74 (1997) 655.
- [5] M. Yin, M.-F. Joubert, J.-C. Krupa, *J. Alloys Compd.* 260 (1997) 64.
- [6] M. Yin, M.-F. Joubert, J.-C. Krupa, *J. Lumin.* 75 (1997) 221.
- [7] P.J. Deren, J.-C. Krupa, M. Yin, M.-F. Joubert, W. Strek, *Spectrochim. Acta, Part A: Mol. Spectrosc.* 54A (13) (1998) 2105.
- [8] P.J. Deren, J.-C. Krupa, W. Strek, *J. Alloys Compd.* 300–301 (2000) 18.
- [9] M. Yin, P.J. Deren, M.-F. Joubert, J.-C. Krupa, *Yuanzi Yu Fenzi Wuli Xuebao* 18 (1) (2001) 4.
- [10] P.J. Deren, M.-F. Joubert, J.-C. Krupa, R. Mahiou, M. Yin, *J. Alloys Compd.* 341 (2002) 134.
- [11] W.T. Carnall, Argonne National Laboratory, Report ANL-89/39, IL, USA, November 1989.