1.064 μm multiphoton laser-induced fluorescence and dissociation of tetrakis-(dimethylamino) titanium(IV)

M. Matti Maricq and Chaitanya K. Narula

Research Staff, Ford Motor Company, P.O. Box 2053, Drop 3083, Dearborn, MI 48121, USA

Received 25 July 1991

Irradiation of $Ti[N(CH_3)_2]_4$ by the 1.064 μm line of a pulsed Nd:YAG laser has been found to produce an intense visible emission due to multiphoton absorption and subsequent dissociation by this species and/or its decomposition products. At low pump intensities a broad and featureless emission is observed over the 250–700 nm range. As the intensity is increased structure corresponding to Ti and Ti^+ fluorescence appears in the emission spectrum. The emission decays as a double exponential with time constants of approximately 0.25 and 1.2 μs. Mass spectroscopic analysis reveals dimethylamine, tetramethylhydrazine and bis-(dimethylamino)methane amongst the dissociation products along with an insoluble residue.

1. Introduction

On one hand, there is currently considerable interest in the laser-assisted processing of materials [1]. Applications range from the laser-induced conversion of precursor molecules into thin films [2] to the laser-driven synthesis of silicon nitride, silicon carbide, and titanium boride powders [3–5]. On the other hand, there is a growing use of tetrakis-(dimethylamino) titanium(IV) (hereafter referred to as titanium amide) as a precursor in the formation of titanium nitride (TiN) coatings via methods ranging from polymer precursor processing [6,7] to chemical vapor deposition [8]. It is evident that laser-assisted formation of titanium nitride films from titanium amide is an interesting issue. Toward this end, the purpose of the present paper is to report the photophysical and photochemical effects of pulsed 1.064 μm radiation on neat $Ti[N(CH_3)_2]_4$. A future contribution will describe laser-assisted formation of TiN coatings on metal oxide particles.

The use of multiphoton dissociation to produce chemically reactive species is not a new one. The majority of previous work concerns infrared multiphoton dissociation (IRMPD) by CO_2 laser radiation at 10.6 μm. For example, Francisco and co-workers have examined the laser-induced fluorescence spectra [9] of CF_2O and CF_3O radicals produced from the IRMPD of bis-trifluoromethyl peroxide in an effort to understand the dissociation mechanism.

Because of the small energy per photon of CO_2 laser radiation, IRMPD at this wavelength usually relies on the precursor molecule having a vibrational band nearly resonant with 10.6 μm radiation. For example the laser synthesis of silicon nitride and carbide powders takes advantage of the strong absorption by SiH_4, or $(Me_3Si)_2NH$, at 10.6 μm to drive the required chemical reactions [3,4]. In this respect the present work is different. An Nd:YAG laser photon has nearly ten times the energy of a CO_2 laser photon; however, its frequency is in a region of the electromagnetic spectrum lying between the usual molecular vibrational and electronic transition energies and it is rare to find a molecule which absorbs strongly in this region.

One of the characteristics of the 1.064 μm irradiation of titanium amide is the appearance of intense visible emission. Visible emission arising in IRMPD experiments has also been previously reported. Karlov [10] has observed a pale yellow fluorescence from the CO_2 laser multiphoton dissociation of BCl_3, probably arising from the $^2B_1$ to $^2A_1$ transition in BCl_2. Rockwood and co-workers [11] have further observed a deep red chemiluminescence from the multiphoton dissociation of BCl_3 in a mixture with H_2S and have attributed it to an ex-

Elsevier Science Publishers B.V.

cited state of BCl_2. The present work reports the observation of a broad continuum emission ranging from 250 to 700 nm when titanium amide is pumped by the fundamental frequency of an Nd:YAG laser and ascribes this to emission from $Ti[N(CH_3)_2]_4$ and/or its decomposition products. At high laser intensity, emission from Ti and Ti^+ is observed, indicating the dissociation of up to four Ti–N bonds by 1.064 μm photons.

2. Experimental

The apparatus used to measure fluorescence from the multiphoton dissociation of $Ti[N(CH_3)_2]_4$ consists of a sample cell, two Nd:YAG lasers operating on the 1.064 μm fundamental wavelength, and a low resolution monochromator with a gated diode array detector. The sample cell is constructed of a 2.4 cm diameter by 94 cm long Pyrex tube with a 25 cm long cross member and an observation window located ≈20 cm from the top and respectively designated as the z, y, and x directions. The cell is charged, under 1 atm of nitrogen or argon, with approximately 0.5–2 ml of titanium amide. The 1.064 μm output of the first Nd:YAG laser is directed through a quartz window and along the vertical, z, axis of the cell, finally impinging the sample. The function of this laser is to flash vaporize the titanium amide and thereby produce a steady state concentration of these molecules throughout the cell. Note, though, that this laser also induces fluorescence and dissociation of the titanium amide along its beam path.

Radiation from the second Nd:YAG laser is directed along the y direction through the cross tube and its power is monitored by a Scientech power meter. In some experiments a 1 m focal length lens is used to reduce the beam diameter in the interaction region to ≈4 mm from its normal value of ≈7 mm. Assuming a pulse width of 9 ns, this results in a maximum intensity of 440 MW cm^{-2} in the interaction zone. Fluorescence generated by the second laser exits perpendicular to both laser beams through a quartz observation window and is focused by a 10 cm focal length lens onto the slits of a 0.32 m monochromator (Instruments SA HR320). The light is dispersed by a 147 groove/mm grating blazed at 300 nm and recorded by a gated, intensified, diode array detector (Princeton Instruments IPDA-700SB detector and ST1000 controller). The intensifier is triggered by laser 2 (laser 1 in single laser experiments) through a variable delay generator having a time resolution of 250 ns. The spectra are calibrated against the emission spectrum of a low pressure Hg lamp.

After approximately 10^5 laser pulses an analysis of the decomposition products was performed. Undecomposed titanium amide was recovered by distillation under vacuum and repeated washing with hexane. The volatile components were collected and analyzed via NMR and GC-mass spectroscopy. The remaining insoluble residue was examined by infrared spectroscopy. One portion was fired at 800°C in an N_2 atmosphere and another at 1100°C under NH_3, with the resulting powders analyzed by X-ray diffraction.

$Ti[N(CH_3)_2]_4$ was prepared according to a literature procedure [12] and all sample handling was carried out under rigorously anhydrous conditions.

3. Results

Irradiating titanium amide with unfocused, Q-switched, 1.064 μm pulses produces a broadband and intense visible emission along the path traversed by the laser beam within the sample cell. This emission, however, does not appear instantaneously. For pulse energies below 0.2 J/pulse, no emission is observed. At approximately 0.3 J/pulse relatively weak emission is observed from the liquid, which slowly begins to change from its normally yellow color to black. By roughly 0.7 J/pulse one begins to observe fluorescing vapors ascending the sample tube. After a time ranging from seconds to minutes the laser beam path along the entire cell length shows a bright visible emission. This incubation time depends on both laser power and buffer gas pressure, being shorter for higher pulse energies and at lower buffer gas pressures. The incubation period is attributed to the time required for irradiation by laser 1 to produce a steady state vapor phase concentration of titanium amide by flash vaporization of the liquid.

The emission color depends on the intensity of the irradiation, changing from pink to white as the pulse energy is increased. Threshold for observing emis-

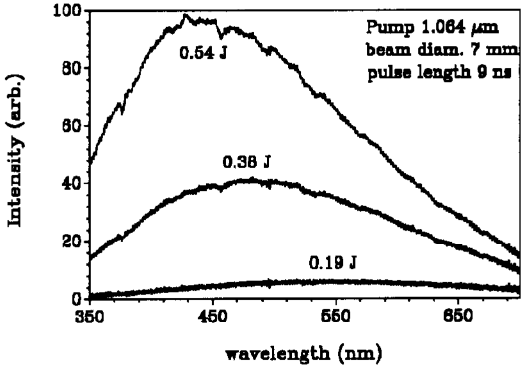


Fig. 1. Power dependence of the fluorescence spectra. The spectra were recorded within 250 ns of the pulse from laser 2, which was unfocused.

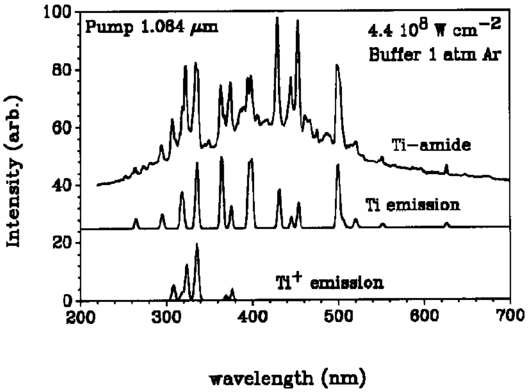


Fig. 2. Comparison of the titanium amide fluorescence spectrum with atomic emission lines from Ti and Ti^+.

sion is approximately[1] 1.5×10^7 W cm^{-2}. Fig. 1 shows that above this threshold there appears a broad and relatively featureless emission band which shifts to the blue as the pump intensity is increased. At 5.4×10^7 W cm^{-2} the maximum is at approximately 550 nm, but it shifts to 450 nm at 1.6×10^8 W cm^{-2} and begins to show signs of structure.

When the laser intensity is increased to 4.4×10^8 W cm^{-2}, by slightly focusing the beam to approximately 4 mm diameter, the spectrum shown in the top trace of fig. 2 is observed. The principal features are well reproduced by the atomic emission lines from Ti and Ti^+. The comparison spectra in fig. 2 were obtained by generating a stick spectrum from about 40 and 30 of the strongest lines respectively for Ti and Ti^+, using the frequencies and intensities complied by Meggers et al. [13], and convoluting the result with a Gaussian lineshape having a full-width at half height of 3.3 nm to account for the resolution of our spectrometer.

The observation of emission at 2 to 3 times the pump frequency and the dissociation/ionization of titanium amide to Ti and Ti^+, clearly suggest a multiphoton process. As fig. 3 illustrates, the dependence of the emission intensity on laser power is well fit by a power law of the form

$$I=AP^{\gamma}, \qquad (1)$$

where A is a constant. These results were obtained from experiments using an unfocused laser beam; thus the fluorescence spectra had bandshapes such as depicted in fig. 1 as opposed to fig. 2. Each point in fig. 3 represents the integrated intensity over a bandwidth of 10 nm at the indicated wavelength. At 650 nm, the fluorescence intensity shows an essentially quadratic dependence on pump power, whereas, at 375 nm the intensity dependence becomes cubic. This is consistent with the fact that 650 nm is accessible by two 1.064 μm photons, while three are required to reach 375 nm. At wavelengths between 375 and 650 nm γ takes on values intermediate between 2 and 3. The integrated emission has a power law depen-

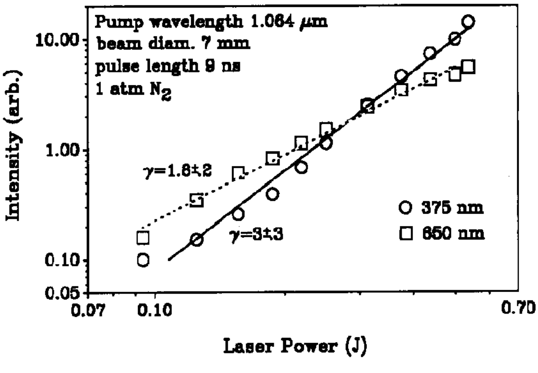


Fig. 3. Dependence of titanium amide fluorescence on laser intensity. The slopes are obtained from a nonlinear least squares fit of eq. (1) to the data, as opposed to a linear regression of the log–log plot, in order that the weighting of the errors in emission intensities and therefore the errors in γ, be more realistically represented.

---

[1] This is for an unfocused, $d=7$ mm, beam with a Q-switched pulse length of $t_p=9$ ns.

dence on laser power with an exponent of $\gamma \approx 2.5$.

The appearance of Ti and Ti^+ emission lines, at the higher laser intensities, also follows a nonlinear dependence on pump power. Accurate values of γ are difficult to obtain because the atomic emission is superimposed on a broad background fluorescence; however, rough estimates place γ in the range of 2–3.5 for a variety of the peaks shown in fig. 2.

In a separate series of (single laser) experiments a dilute solution of titanium amide in hexane was irradiated at 1.064 μm. As with the gas phase experiments, visible emission was observed from the solution. This fluorescence spectrum essentially reproduces the gas phase results at wavelengths longer than 480 nm; the emission is attenuated at shorter wavelengths because of the strong titanium amide absorption band which begins in this region. In this case the dependence of integrated emission on laser intensity is fit by a power law with $\gamma = 3.5$.

Fluorescence from laser excitation of the titanium amide appears within the 250 ns time resolution of the gating electronics to the diode array. It then disappears in a double exponential decay, as shown by fig. 4. The points in this figure are obtained by measuring the integrated emission as a function of delay time from the pump laser pulse. The fast part of the decay accounts for an approximately tenfold decrease in emission intensity and has a time constant of $\tau_f \approx 260$ ns, which represents an upper limit on account of the time resolution of our spectrometer.

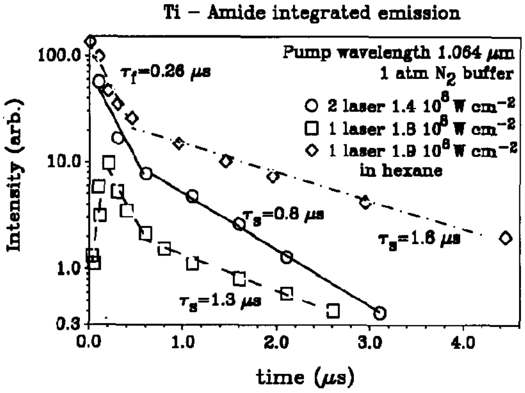


Fig. 4. Time dependence of the integrated emission from titanium amide under a variety of experimental conditions. The time constants are obtained from a piece-wise linear least squares fit of $\ln(I)$ to t.

The slow component has a time constant that varied over the range of 0.8 to 1.6 μs depending on experimental run. The slow decay is likely due to collisional quenching and the variation presumably arises from differences in buffer gas pressure and/or steady state vapor phase titanium amide concentration. A more precise determination of decay rate was not pursued at this time, the main point being established that at least one component of the emission survives on the order of 10^4 buffer gas collisions. Interestingly enough, the slow decay component observed for experiments carried out in hexane solution, $\tau_s = 1.3$ μs, falls within the range of gas phase results.

A different view of the time dependence of the emission is provided by the time resolved spectra displayed in fig. 5. The atomic emission features are observed to decay within the 250 ns resolution of our instrument, although the decay rates are not uniform for all lines. This time scale is consistent with atomic radiative lifetimes and collisional quenching rates. The broad background emission decreases more slowly with time and concomitantly shifts to red. Such a shift is consistent with vibrational relaxation taking place in the upper electronic state of the emitting species.

After a large number of laser pulses (approximately 2×10^5 pulses from laser 1) volatile components of the sample were removed by bulb to bulb fractional distillation and separated from unreacted titanium amide, leaving a black insoluble residue.

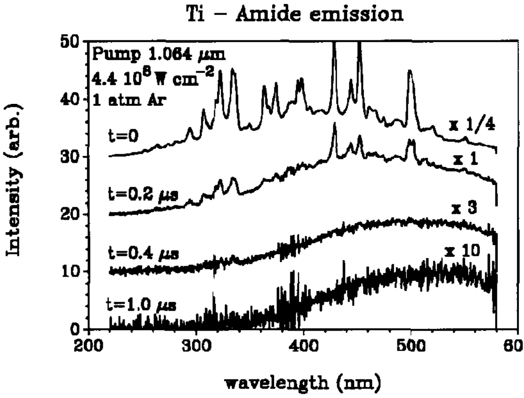


Fig. 5. Time resolved titanium amide fluorescence spectra. Note the change in scale factor as time increases.

The volatile species were analyzed by GC-mass spectroscopy and by ^{1}H NMR. The NMR spectrum consisted of two peaks: one at 1.86 ppm due to dimethylamine and the other at 1.7 ppm arising from tetramethylhydrazine. The GC-mass spectrum showed that, in addition to these two species, the volatile component contained bis-(dimethylamino)methane, ethane, and trace amounts of unidentified species. An infrared spectrum of the insoluble residue showed some features in the 2800–3000 cm^{-1} region, suggesting the presence of hydrocarbon groups. After firing the residue at 800°C in a nitrogen atmosphere, the X-ray powder diffraction showed peaks at 2θ (intensity) values of 36.8 (47), 42.9 (100), 62.1 (64), 74.4 (21) and 78.5 (16) corresponding to TiN and 36.3 (41), 42.0 (64), 61.0 (34), 73.1 (18) and 76.8 (10) corresponding to TiC. Firing the residue at 1100°C in an ammonia atmosphere yielded an X-ray powder diffraction pattern in excellent agreement with the reported TiN diffraction pattern (JCPD # 38,1420).

4. Discussion

This section draws, from the above results, some conclusions regarding the 1.064 μm photochemistry of titanium amide. One of the primary questions is: what species is responsible for the multiphoton absorption of 1.064 μm photons and the subsequent fluorescence? Our initial experiments, using a single laser, could not elucidate this, because they could not distinguish between the fluorescence originating from gas phase multiphoton absorption versus the possibility that hot decomposition products arising from laser pyrolysis of liquid titanium amide cause the visible emission. One piece of evidence supporting the multiphoton absorption mechanism is the formation of tetramethylhydrazine, since this is normally not found as a pyrolysis product. More direct evidence is provided by the observation of emission, including Ti and Ti$^+$ emission, from the beam path of laser 2, which traverses only the vapor phase; however, this does not unequivocally ascribe the emission to $Ti[N(CH_3)_2]_4$. The species responsible for the multiphoton absorption could be titanium amide itself, or a laser-induced dissociation or pyrolysis fragment vaporized from the liquid.

The fact that Ti and Ti$^+$ emission is observed (see fig. 2) indicates that the absorbing molecule is a titanium compound. The existence of Ti–N bonds appears to play an important role in the multiphoton absorption since bright visible emission, similar to that from $Ti[N(CH_3)_2]_4$, is observed from the path traced by the laser beam upon both the irradiation of poly(amido) titanium [#2] powder and titanium nitride. In contrast the irradiation of $TiCl_4$ and $Ti(i\text{-}C_3H_7O)_4$ does not yield any visible emission [#3], nor is emission observed from $B[N(CH_3)_2]_3$ or $Si[N(CH_3)_2]_4$.

The species which absorbs 1.064 μm photons is a long-lived one. Evidence for this is provided by the following experiment. Laser 1 was used to irradiate a sample of titanium amide for several minutes until a steady state visible fluorescence was observed from the entire length of the cell, and was then turned off. The integrated fluorescence induced by laser 2 was then measured at various times over the course of 160 min. The results reveal an exponential decrease in fluorescence intensity with a half life of 29 min. This sufficiently long that diffusion and removal by sticking to the wall could account for the decrease in intensity with time. Therefore, if not titanium amide itself, a stable, long-lived, decomposition product which is flash vaporized from the liquid sample must be responsible for the multiphoton absorption and subsequent fluorescence.

Since it is reasonable to assume that titanium amide does undergo multiphoton dissociation, some of its properties are worth considering. Titanium amide has tetrahedral coordination, but belongs to D_{2d} symmetry owing to the lack of free rotation about the Ti–N bond [14]. The nitrogen atoms are trigonal planar and the lone pair orbitals are, by photoelectron spectroscopy [14], the highest occupied molecular orbitals. Infrared studies [15] and core electron [16] binding energies suggest that these orbitals contribute additional $p\pi \rightarrow d\pi$ bonding to the N–Ti σ bond. The N–Ti σ bonding orbitals them-

---

[#2] This is a solid polymer formed from the reaction of $TiCl_4$ with $(Me_3SI)_2NH$. It consists of Ti–NH–Ti bridges capped by Ti–Cl and Ti–NHSiMe$_3$ group. C.K. Narula, patent application. # 07-625180, 12/90.

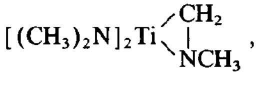
[#3] If the laser beam is sharply focused to the point of causing electrical breakdown, Ti and Ti$^+$ fluorescence are observed from $TiCl_4$.

selves lie about 3 eV lower in energy. The visible/UV spectrum of titanium amide shows a strong absorption beginning at 520 nm and extending to the blue which is consistent with an electronic transition from the nitrogen lone pair orbital to an unoccupied Ti 3d orbital. There is also a series of weak bands, with cross section less than 1.9×10^{-22} cm^2 in the range between 900 and 1500 nm.

The change in color from yellow/orange to brown/black upon the irradiation of neat $Ti[N(CH_3)_2]_4$ by 1.064 μm light provides some evidence that the molecule undergoes multiphoton dissociation. The mean $Ti-NMe_2$ bond dissociation energy has been determined from the heat of alcoholysis to be 77 kcal mol^{-1} [17]; thus three 1.064 μm photons have sufficient energy to break the bond. It is possible that the states associated with the weak absorption bands in the 900 to 1500 nm region could enhance such a tree-photon process. The change in color of the liquid significantly enhances the absorption coefficient at 1.064 μm and introduces the possibility of flash vaporization and pyrolysis of the titanium amide. This accounts for the observation of fluorescing gases slowly ascending the sample tube.

If it were not for two facts, one could ascribe the broad visible emission spectrum, shown in fig. 1, to a three-photon transition from the nitrogen lone pair to the Ti 3d orbital in titanium amide followed by fluorescence back to the ground electronic state. The cubic laser power dependence measured at 375 nm would support such a hypothesis; however, the quadratic dependence of the fluorescence at 650 nm suggests a two-photon absorption. Furthermore, the fact that the fluorescence intensity not only decreases as a function of laser power, but also shifts to the red (fig. 1), indicates that the observed emission does not arise from a single multiphoton process.

The simplest hypothesis, consistent with the results described in section 3, is that laser 1 is responsible for multiphoton dissociation and/or pyrolysis of titanium amide and flash vaporization of titanium amide and its decomposition products. This eventually leads to a steady state distribution of gas phase $Ti[N(CH_3)_2]_n$ species with $n=1-4$, arising from multiphoton dissociation, and/or



$$[(CH_3)_2N]_2Ti\begin{matrix}\diagup CH_2\\ \quad|\\ \diagdown NCH_3\end{matrix},$$

from laser-induced pyrolysis [18], which are entrained in the 1 atm of N_2 or Ar buffer gas. At low intensities, laser 2 induces multiphoton absorption and fluorescence in these molecules leading to the broad featureless component of the visible emission. Higher laser intensities lead, in addition, to multiphoton dissociation of $Ti[N(CH_3)_2]_n$, eventually yielding Ti and Ti^+. Finally, the various amido titanium radicals recombine and polymerize to form the insoluble, grey/black, coating that is found to form on the walls of the sample tube.

5. Conclusion

Pulsed 1.064 μm irradiation of neat titanium amide has been found to produce multiphoton laser-induced fluorescence and dissociation of these molecules. This is corroborated by the nonlinear dependence of the fluorescence spectra on laser power. Observation of the decomposition products dimethylamine and tetramethylhydrazine on one hand, and the lack of dissociation in $TiCl_4$, $Ti(i\text{-}C_3H_7O)_4$, and $Si[N(CH_3)_2]_4$ samples on the other, indicates that the Ti–N bond is the one that is broken. At an intensity of 4.4×10^8 W cm^{-2} up to four bonds are broken, as evidenced by emission spectrum showing lines assignable to Ti and Ti^+, in a process requiring the absorption of approximately 15 photons.

References

[1] P. Herman, Chem. Rev. 89 (1989) 1323.

[2] A.P. Magee, P.R. Strutt and K.E. Gonsalves, Chem. Mater. 2 (1990) 232.

[3] J.D. Casey and J.S. Haggerty, J. Mater. Sci. 22 (1987) 737; Y. Suyama, R.M. Marra, J.S. Haggerty and H.K. Bowen, Am. Ceram. Soc. Bull. 64 (1985) 1356.

[4] G.W. Rice, J. Am. Ceram. Soc. 69 (1986) C183.

[5] M. Cauchetier, O. Croix and M. Luce, Advan. Ceram. Mater. 3 (1988) 548.

[6] G.M. Brown and L. Maya, J. Am. Ceram. Soc. 71 (1989) 78.

[7] G. Mignami and D. Seyferth, Gov. Rep. Announce. Index (US) 88 (1988) 827, 109; Chem. Abs. 109 (1988) 214, 916.

[8] R.M. Fix, R.G. Gordon and D.M. Hoffman, J. Am. Chem. Soc. 112 (1990) 7833.

[9] J.S. Francisco and Z. Li, preprint;
Z. Li and J.S. Francisco, Chem. Phys. Letters, in press.
[10] N.V. Karlov, Appl. Opt. 13 (1974) 301.
[11] S.D. Rockwood, Chem. Phys. 10 (1975) 453;
S.D. Rockwood and J.W. Hudson, Chem. Phys. Letters 34 (1975) 542.
[12] D.C. Bradley and I.M. Thomas, J. Chem. Soc. (1960) 3857.
[13] W.F. Meggers, C.H. Corliss and B.F. Scribner, Tables of spectral line intensities, NBS Monograph 145, part 1 (1975).
[14] S.G. Gibbins, M.F. Lappert, J.B. Pedley and G.J. Sharp, J. Chem. Soc. Dalton Trans. (1975) 72.
[15] D.C. Bradley and M.H. Gitlitz, J. Chem. Soc. A (1969) 980.
[16] R.A. Andersen, D.B. Beach and W.L. Jolly, Inorg. Chem. 24 (1985) 4741.
[17] M.F. Lappert, D.S. Patil and J.B. Pedley, J. Chem. Soc. Chem. Commun. (1975) 830.
[18] Y. Takahashi, N. Onoyama, Y. Ishikawa, S. Motojima and K. Sugiyama, Chem. Letters (1978) 525.