which thermochemical data were not in fact available. Now that genuine AM1 parameters are available for sulfur, the AM1 and PM3 results for sulfur compounds are seen to be comparable. We have always avoided changes in our procedures unless and until they lead to major improvements. As a result, there is only one version of each, ensuring that results obtained in different laboratories are comparable. This unfortunately is not true in the ab initio area because the use of different basis sets usually precludes such comparisons.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AF89-0179), the Robert A. Welch Foundation (Grant F-126), and the National Science Foundation (Grant CHE 87-12022).

Registry No. S, 7704-34-9.

Notes

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 105. Redox Reactions of Nitrosonium-Bound Chromium(I), $Cr^I(NO^+)$[1]

Amrit K. Jhanji and E. S. Gould*

Received April 23, 1990

Ligation by the nitrosonium ion, NO^+, can stabilize the low oxidation states of a number of transition metals.[2] The prototype example is the "brown ring" cation $(FeNO)^{2+}$, which has been shown[3] to be a NO^+ complex of Fe(I) rather than a NO complex of Fe(II). Similarly, complexes appearing to be NO^+ derivatives of V(−I) and Mo(II) have been described.[4]

The unusual oxidation state, chromium(I), has become accessible through nitrosonium coordination. The cyano complex, $[Cr^I(NO^+)(CN)_5]^{3-}$, was reported in 1959 by Griffith,[4] the aqua complex, $[Cr^I(NO^+)(H_2O)_5]^{2+}$, was characterized by Ardon in 1962,[5] and a related $Cr^I(NO^+)$ chelate, formed from the bidentate anion of 2-ethyl-2-hydroxybutanoic acid, was prepared by Rajasekar in 1983.[6] A greatly improved synthesis of the pentaaquo cation was described by Armor in 1973.[7] Each of these complexes exhibits a magnetic moment and spectral features characteristic of a low-spin $(t_{2g})^5$ derivative.[6,8] Solutions of such complexes survive for several hours at ambient temperatures, and with care, crystalline derivatives may be isolated.[5] Yet, aside from a detailed study of the reaction of $[Cr(NO)(H_2O)_5]^{2+}$ with Cr^{2+} by Armor,[7] little is known concerning the chemistry of $Cr^I(NO^+)$ species. Although the $[Cr(NO)(H_2O)_5]^{2+}$ cation has two sites where redox reactions may, in principle, occur, we find that it is quite resistant to all but the most powerful oxidants and reductants. The present study deals with reactions of this complex with the oxidants BrO_3^- ($E° = 1.52$ V) and IO_4^- (1.7 V) and with the reductant U^{3+} (−0.61 V).[9]

Experimental Section

Materials. Sodium bromate (Sargent) and sodium periodate (Alfa) were used as received. Sodium perchlorate solutions (for use in kinetic experiments) were prepared by careful neutralization of $NaHCO_3$.

Table I. Stoichiometries of the Reactions of $[Cr(NO)(H_2O)_5]^{2+}$ with Inorganic Redox Reagents (0.5 M $HClO_4$)

A. Reactions with IO_2^- (450 nm)

$10^3 \times [Cr(NO)^{2+}]$	$10^3 \times [IO_4^-]$	$10^3 \times \Delta[Cr(NO)^{2+}]$	$\Delta[Cr(NO)^{2+}]/\Delta[IO_4^-]$
1.50	0.50	0.40	0.80
1.50	1.00	0.90	0.90
1.50	1.25	1.23	0.98
1.50	1.50	1.43	0.95

B. Reactions with BrO_3^- (325 nm)

$10^3 \times [Cr(NO)^{2+}]$	$10^3 \times [BrO_3^-]$	$10^3 \times \Delta[Cr(NO)^{2+}]$	$\Delta[Cr(NO)^{2+}]/\Delta[BrO_3^-]$
10.5	4.0	5.9	1.46
10.5	7.0	9.8	1.39

C. Reactions with U(III) (450 nm)

$10^3 \times [Cr(NO)^{2+}]$	$10^3 \times$ [U(III)]	$10^3 \times \Delta[Cr(NO)^{2+}]$	$\Delta[Cr(NO)^{2+}]/\Delta$[U(III)]
6.40	4.17	1.77	0.42
5.60	6.77	4.14	0.61
6.50	7.22	3.59	0.49
3.80	3.65	1.72	0.47

Table II. Variation, with Acidity, of the Spectrum of $[Cr(NO)(H_2O)_5]^{2+}$ (25 °C)[a]

$10^6[H^+]$, M	R_{obsd}[b]	R_{calcd}[c]	$10^6[H^+]$, M	R_{obsd}[b]	R_{calcd}[c]
316	1.45	1.41	6.2	0.88	0.85
72	1.25	1.30	3.9	0.86	0.78
17.3	0.96	1.06	2.5	0.83	0.73
10.9	0.93	0.96	0.04	0.61	0.61

[a] $[H^+]$ was adjusted by addition of $HOAc/OAc^-$ buffer or tris(hydroxymethyl)aminomethane (Tris). [b] Observed ratio of absorbances at 448 and 380 nm. [c] Absorbance ration (448/380 nm) calculated by using eq 1, with R_B taken as 0.61, R_{BH} as 1.45, and K_A as 1.49×10^{-5} M.

Uranium(III) solutions were prepared by dissolving dry U_3O_8 in warm dilute $HClO_4$ and then reducing with Zn(Hg) under N_2 until the spectrum of the resulting olive green solution remained invariant.[10]

Solutions of $[Cr(NO)(H_2O)_5]^{2+}$ were prepared[5] by reducing 0.6 M $Cr(ClO_4)_3$ (Alfa) in 1 M $HClO_4$ with zinc amalgam under N_2 and then adding the resulting $Cr(ClO_4)_2$ solution (6 mL) dropwise to 150 mL of water, which was stirred and continuously saturated with NO.[11] The NO flow was then switched to N_2 to expel the excess NO, and the solution was absorbed onto a column of Dowex 50W-X8 (H^+ form). The desired complex was eluted with 0.5 M $HClO_4$. Solutions were standardized spectrophotometrically ($\epsilon_{449}^{max} = 120$ M^{-1} cm^{-1}).[5]

Stoichiometric Studies. The stoichiometries of the reactions of $Cr(NO)^{2+}$ with IO_4^- and BrO_3^- were determined in 0.5 M $HClO_4$ by adding known deficiencies of the oxidants to an excess of the chromium complex, waiting until completion of the reaction, and then estimating the decreases in absorbance due to $Cr(NO)^{2+}$. Measurements were made at 450 nm for the I(VII) reactions and 325 nm for Br(V). The resulting changes were compared with those occurring on treatment with excess oxidant. The stoichiometry of the reaction with U(III) was determined

---

[1] Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] Reviews: (a) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. (b) Bottomley, F. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1989; Vol. 2, p 115. (c) Mingos, D. M. P.; Sherman, D. J. *Adv. Inorg. Chem.* **1989**, *34*, 293.

[3] Griffith, W. P.; Lewis, J.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3493.

[4] Griffith, W. P.; Lewis, J.; Wilkinson, G. *J. Chem. Soc.* **1959**, *872*, 1632.

[5] Ardon, M.; Herman, J. I. *J. Chem. Soc.* **1692**, 507.

[6] Rajasekar, N.; Subramaniam, R.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 971.

[7] Armor, J. N.; Buchbinder, M. *Inorg. Chem.* **1973**, *12*, 1086.

[8] Griffith, W. P. *J. Chem. Soc.* **1963**, 3286.

[9] Latimer, W. M., *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; Chapters 5 and 21. The potentials listed refer to the conversions $2BrO_3^- \rightarrow Br_2$, $H_5IO_6 \rightarrow HIO_3$, and $U^{4+} \rightarrow U^{3+}$, each in 1 M H^+. Complications in the I(VII) system due to the equilibrium between IO_4^- and its hydrated form $H_4IO_6^-$ appear to play no part in this study.

[10] Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330.

[11] Blanchard, A. A. *Inorg. Synth.* **1946**, *2*, 126.

Table III. Representative Kinetic Data for the Reactions of $Cr(NO)(H_2O)_5^{2+}$ with Bromate, Periodate, and Uranium(III)[a]

bromate reactions[b]			periodate reactions[c]			uranium(III) reactions[d]			
$[BrO_3^-]$	$[H^+]$	k^e	[I(VII)]	$[H^+]$	k^e	$10^3[Cr(NO)^{2+}]$	10^4[U(III)]	$[H^+]$	k^e
0.025	0.65	1.88	0.010	0.35	1.10				
0.050	0.65	2.0	0.025	0.35	1.08	3.3	6.5	0.60	5.2
0.020	0.95	3.2	0.010	0.95	0.26	5.2	6.5	0.60	4.8
0.020	0.75	2.2	0.010	0.75	0.35	6.5	6.5	0.60	4.6
0.020	0.50	1.45	0.010	0.55	0.47	7.7	6.5	0.60	4.9
0.020	0.35	0.98	0.010	0.45	0.72	6.5	13.0	0.60	4.8
0.020	0.25	0.70	0.010	0.25	1.30	6.5	6.5	0.95	4.8
			0.010	0.15	2.2	6.5	6.5	0.80	4.7
			0.010	0.100	3.3	6.5	6.5	0.70	4.8
			0.010	0.080	4.8	6.5	6.5	0.10	4.9
			0.010	0.060	5.7				

[a] Reactions at 25 °C; $\mu = 1.0$ M ($HClO_4$–$NaClO_4$). [b] $[Cr(NO)^{2+}] = 5 \times 10^{-4}$–$1 \times 10^{-3}$ M; 470 nm. [c] $[Cr(NO)^{2+}] = 5 \times 10^{-4}$–$1 \times 10^{-3}$ M; 450 nm. [d] 350 nm. [e] Bimolecular specific rates ($M^{-1}\ s^{-1}$).

by generating this reductant under N_2 in a closed cell,[10] estimating its concentration at 522 nm ($\epsilon = 147\ M^{-1}\ cm^{-1}$), and then adding a known excess of $Cr(NO)^{2+}$. The U(IV) formed was then oxidized to U(VI) with ClO_3^- (which does not oxidize $Cr(NO)^{2+}$ appreciably under these conditions), and the unreacted Cr(I) complex was estimated at 450 nm. Results are summarized in Table I.

Examination of Products. The chromium reaction product in each case exhibited ion-exchange behavior and spectral features characteristic of $Cr(H_2O)_6^{3+}$.[12] Solutions from periodate oxidations displayed absorbance peaks at 357, 370, and 386 nm, corresponding to those of authentic aqueous HNO_2, and gave positive tests for iodate but did not contain detectable concentrations of iodine or iodide. Solutions from the bromate oxidations gave positive tests for both bromide and nitrate. Solutions from U(III) reductions tested positively for NH_3OH^+ when treated with mixtures of Fe(III), H_2O_2, and formaldehyde.[13]

Kinetic Measurements. Rates were estimated from measurements of absorbance changes on a Beckman Model 5260 recording spectrophotometer. Ionic strength was fixed by addition of $NaClO_4$, and acidities were regulated with $HClO_4$. Oxidations by periodate (monitored at 450 nm) and by bromate (followed at 470 nm) were carried out under pseudo-first-order conditions with at least a 10-fold excess of oxidant, whereas reductions by U(III) (observed at 350 nm) were run with $Cr(NO)^{2+}$ in large excess. Conversions were followed to at least 98% completion. All reactions were first order in the two redox partners. Specific rates from replicate runs, obtained from logarithmic plots of absorbance differences against reaction time, agreed to within 8%. Examination of kinetic profiles gave no indication of intermediates formed or destroyed on a time scale comparable to that of the primary reaction. Moreover, no sharp drop in absorbance occurred immediately after adding the oxyhalogen reagents, thus ruling out the rapid formation of a partially oxidized chromium species.

The $Cr(NO)^{2+}$ ion did not react at a measurable rate with the oxidants chlorate, chlorite, hydrogen peroxide, and peroxydisulfate under our conditions nor with the reductants europium(II), vanadium(II), mercaptoacetic acid, bisulfite, phosphite, and hypophosphite.

Estimation of the pK_A of $[Cr(NO)(H_2O)_5]^{2+}$. This complex, as eluted from cation-exchange resin with 0.5 M $HClO_4$, underwent a rapid and reversible color change from brown to pink at pH values greater than 5. During this conversion, the absorbance at 448 nm decreased while that at 380 nm grew. The ratio of these absorbances, R, was used to estimate the pK_A of the complex. The relationship[14] is (1) in which R_{BH} and R_B

$$R = \frac{R_B K_A + R_{BH}[H^+]}{K_A + [H^+]} \qquad (1)$$

represent the absorbance ratios for the protonated and deprotonated forms of this complex. Absorbance data (Table II) led to a K_A value of $(1.5 \pm 0.3) \times 10^{-5}$ M ($pK_A = 4.8$, 25 °C, $\mu = 0.5$ M).

Results and Discussion

Variation of the spectrum of $[Cr(NO)(H_2O)_5]^{2+}$ within the pH range 3.5–7.6 (Table II) leads to a pK_A value of 4.8. The cation is thus a weaker acid than $Cr(H_2O)_6^{3+}$ ($pK_A = 3.8$)[15] but is far more acidic than one would expect for an aquated complex of a unipositive metal center in the absence of the strongly electron-attracting nitrosonium group. Within the acidity range taken for rate measurements, BrO_3^- exists predominantly in the anionic form,[16] whereas I(VII) is converted very largely to H_5IO_6 (apparent $pK_a = 1.66$).[17]

Stoichiometric experiments (Table I) tell us that 1 mol of $Cr(NO)^{2+}$ consumes very nearly 1 mol of I(VII), $^2/_3$ mol of Br(V), and 2 mol of U(III). These ratios are consistent with net transformations listed as (2)–(4). Positive tests for each of the

$$Cr(NO)^{2+} + H_5IO_6 \rightarrow Cr^{3+} + HNO_2 + IO_3^- + 2H_2O \qquad (2)$$

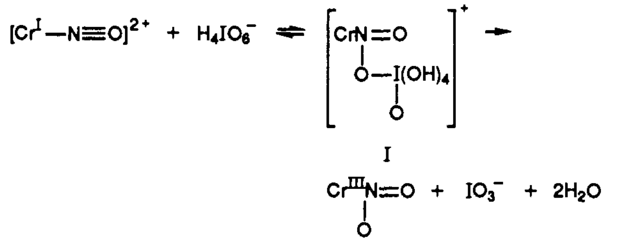
$$3Cr(NO)^{2+} + 2BrO_3^- \rightarrow 3Cr^{3+} + 3NO_3^- + 2Br^- \qquad (3)$$

$$Cr(NO)^{2+} + 2U^{3+} + 4H^+ \rightarrow Cr^{3+} + 2U^{4+} + NH_3OH^+ \qquad (4)$$

indicated products confirm these formulations.

Representative kinetic data appear in Table III. Reductions by U(III) ($k = 4.9 \pm 0.2\ M^{-1}\ s^{-1}$) are seen to be independent of pH within the range considered. The oxidation by periodate exhibits an inverse-acid dependence ($k_{obsd} = (0.31 \pm 0.02\ s^{-1})[H^+]^{-1}$), whereas the reaction with bromate is first order in $[H]^+$ ($k_{obsd} = (3.1 \pm 0.1\ M^{-2}\ s^{-1})[H^+]$).

The rate law for reaction with periodate, a 2e⁻ oxidant, points to a transition state consisting of $Cr(NO)^{2+}$ and $H_4IO_6^-$. We favor a bridged intermediate of type I,[18] which may react, via oxygen atom transfer and an internal metal-to-ligand 2e⁻ shift, to form the nitro-substituted chromium(III) complex II (sequence 5).



(5)

$$II + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} + HNO_2 \quad \text{(rapid)} \qquad (6)$$

Rapid aquation of the latter (reaction 6), to nitrite and Cr^{III}(aq), is in accord with the recognized[19] lability of $Cr^{III}NO_2$ species.

A related path may be envisaged for oxidation by bromate, but here attack by the less basic BrO_3^- anion requires preliminary protonation of the nitrosonium group (reflected in the observed $[H^+]$ dependence). The system is further complicated by the high reactivity of the 2e⁻ and 4e⁻ reduction products, $HBrO_2$ and HBrO, which may also transfer oxygen atoms to bound NO^+. These

---

[12] Laswick, J. A.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3564.

[13] Oddo, G.; Deleo, E. *Ber. Dtsch. Chem. Ges. A* **1936**, *69*, 287.

[14] Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.

[15] Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; p 32.

[16] Choppin, G. R.; Ensor, D. D. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1226. These authors record a pK_A value of −2.3 for $HBrO_3$.

[17] (a) Kren, R. M.; Dodgen, H. W.; Nyman, C. J. *Inorg. Chem.* **1968**, *7*, 446. (b) Crouthamel, C. E.; Hayes, A. M.; Martin, D. S. *J. Am. Chem. Soc.* **1951**, *73*, 82.

[18] Attacks by anions on metal-bound nitrosonium groups have been summarized by McCleverty.[2a]

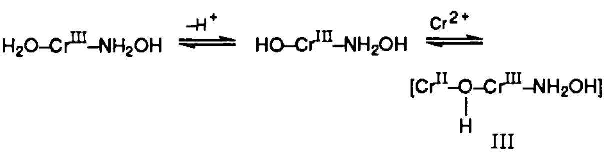
[19] See, for example: Fee, W. W.; Garner, C. S.; Harrowfield, J. N. MacB. *Inorg. Chem.* **1967**, *6*, 87.

reactions must be more rapid than transfer from bromate, for the principal reduction product is Br^-, even when BrO_3^- is taken in excess. In this case, the further rapid oxidation of HNO_2 to NO_3^- accommodates the observed 3:2 stoichiometry.

Reduction by U(III) necessarily involves a pair of 1e⁻ transactions (sequence 7). An internal 2e⁻ shift is needed here as well,

$$[Cr^{I}—N{\equiv}O]^{2+} \xrightarrow{U^{III}} [Cr—N\overset{\bullet}{=}O]^{+} \xrightarrow[3H^{+}]{U^{III}} [Cr^{III}—NH_2OH]^{3+} \quad (7)$$

but we cannot say where in the sequence this occurs. The observed release of uncomplexed hydroxylamine is not wholly expected in view of the recorded[20] very slow aquation of the closely related Cr–N bond in $Cr(H_2O)_5(NH_3)^{3+}$ and the reported[21] persistence of Cr(III) complexes of hydroxylamine in aqueous solution. We suspect that aquation in this instance is catalyzed by traces of Cr(II) present in this strongly reducing solution (sequences 8,9).



$$H_2O–Cr^{III}–NH_2OH \underset{}{\overset{-H^+}{\rightleftharpoons}} HO–Cr^{III}–NH_2OH \overset{Cr^{2+}}{\rightleftharpoons} [Cr^{II}–\underset{\substack{|\\H}}{O}–Cr^{III}–NH_2OH] \quad (8)$$

III

$$III \rightarrow Cr^{III}–OH + Cr^{2+} + NH_2OH \quad (9)$$

In sum, this study underscores the unique ability of the nitrosonium function to stabilize Cr(I), doubtless reflecting the capacity of this group to partake in strong metal-to-ligand back-bonding.[21] When this ligand is altered electronically, by either oxidation or reduction, rapid internal electron transfer generates the familiar tripositive state.

Acknowledgment. We thank Ms. Arla McPherson for technical assistance.

---

(20) Espenson, J. H.; Carlyle, D. W. *Inorg. Chem.* **1966**, *5*, 586. These workers report a half-life period of approximately 3000 h for this aquation at 45 °C.

(21) Ivashkovich, E. M.; Zhelekovskaya, L. M. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 33; *Chem. Abstr.* **1979**, *90*, 145161w.

(22) See, for example: Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* **1966**, *7*, 277.

Contribution from the Department of Chemistry,
University of New Orleans,
New Orleans, Louisiana 70148

Synthesis and Crystal Structure of a Novel Layered Zintl Phase: $K_3Ga_3As_4$

Teresa L. T. Birdwhistell, Edwin D. Stevens,
and Charles J. O'Connor*

Received December 18, 1989

The semiconducting industry is actively searching for new types of semiconducting phases as well as new techniques for the preparation of crystalline and thin-film forms of known semiconducting phases. Of particular interest are the IV and III–V type semiconductors. A great deal of research has been reported on the methods of preparation of III–V type semiconductors.[1] Most of these techniques involve some sort of vapor-phase deposition to form structured films. For example, (AlGa)As/GaAs[2-6] and InP·(InGa/As) and (InGa)(AsP)[7-9] have been deposited via molecular beam epitaxy (MBE) and (AlGa)As/GaAs[10,11] have been prepared via organometallic vapor-phase epitaxy (OMVPE). The usual form of arsenic used for these preparations is AsH_3 or AsR_3 (where R is an organic group).[13,14] Other alternatives involve adducts of Ga–As complexes[15-18] or arsenic–organosilanes.[12] Because of the problems associated with AsH_3, new approaches to the formation of GaAs films are desirable.

Another approach to the synthesis of III–V semiconductors is through the use of I–III–V Zintl phase materials as precursors. The reactivity of Zintl phase materials affords the possibility of solution-phase deposition of semiconducting films and perhaps the layering of metal–semiconductor deposition.[19,20] The reaction of a I–III–V Zintl phase with a III–VII salt (e.g., $GaCl_3$) would produce a III–V phase and a water-soluble alkali-metal halide.

Besides their potential for solution chemistry, the ternary Zintl phase materials are intrinsically interesting. In recent years a large number of crystal structures of ternary Zintl phase materials have been reported.[21-25] These materials display a wide range of structures, from discrete molecular units to one- or two-dimensional polymeric arrays. Despite the wealth of structural information that is unfolding, little is being done to explore the physical and chemical properties of these materials.

We have undertaken the synthesis of a series of I–III–V ternary Zintl phase materials, both as a preliminary step in the investigation of new synthetic routes to the preparation of III–V type semiconductors and for the purpose of investigating their electrical, magnetic, and structural properties. Several I–III–V Zintl phase materials have already appeared in the literature: $KGaSb_2$,[26] $K_3Al_2As_3$,[27] $Na_7Al_2Sb_5$,[28] $Na_2Al_2Sb_3$,[29] and $K_2Al_2Sb_3$.[29] The

---

(1) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. Collins, D. M. Frontiers of Electronic Materials Processing. *AIP Conf. Proc.* **1986**, *138*, 140.

(2) Cho, A. Y.; Casey, H. C. *Appl. Phys. Lett.* **1974**, *25*, 288.

(3) Tsang, W. T.; Logan, R. A.; Salathe, R. P. *Appl. Phys. Lett.* **1979**, *34*, 413.

(4) Fujii, T.; Hiyamizu, S.; Wada, O.; Sugahara, T.; Yamakoshi, S.; Sakurai, T.; Hashimoto, H. *J. Cryst. Growth* **1983**, *61*, 393.

(5) Fujii, T.; Hiyamizu, S.; Yamakoshi, S.; Ishikawa, T. *J. Vac. Sci. Technol.* **1985**, *B3*, 776.

(6) Iwamura, H.; Saku, T.; Kobayashi, H.; Horikoshi, Y. *J. Appl. Phys.* **1983**, *54*, 2692.

(7) Tsang, W. T. *Appl. Phys. Lett.* **1984**, *44*, 288.

(8) Kawamura, Y.; Asahi, H.; Nagai, H. *J. Appl. Phys.* **1983**, *54*, 841.

(9) Masu, K.; Mishima, T.; Hiroi, S.; Konagai, S.; Takahashi, K. *J. Appl. Phys.* **1983**, *53*, 7558.

(10) André, J. P.; Brière, A.; Rocchi, M.; Riet, M. *J. Cryst. Growth* **1984**, *68*, 445.

(11) Hersee, S. D.; Hirtz, J. P.; Baldy, M.; Duchemin, J. P. *Electron. Lett.* **1982**, *18*, 1076.

(12) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. A. *Chem. Mater.* **1989**, *1*, 4.

(13) Leys, M. R. *Chemtronics* **1987**, *2*, 155.

(14) Stringfellow, G. B. *J. Electron. Mater.* **1988**, *17*, 327.

(15) Zaouk, A.; LeBugle, A.; Constant, G. J. *J. Cryst. Growth* **1979**, *46*, 415.

(16) Maury, F.; Constant, G. J.; Fontain, P.; Biberian, J. P. *J. Cryst. Growth* **1986**, *78*, 185.

(17) Maury, F.; Hammadi, A.; Constant, G. J. *J. Cryst. Growth* **1984**, *68*, 88.

(18) Byrne, E. K.; Theopold, K. H. *Science* **1988**, *241*, 332.

(19) Haushalter, R. C. *Angew. Chemie* **1983**, *95*, 560.

(20) Haushalter, R. C.; Krauss, L. J. *Thin Solid Films* **1983**, *102*, 2312.

(21) Schäfer, H. *Annu. Rev. Mater. Sci.* **1985**, *15*, 1.

(22) Schäfer, H.; Eisenmann, B.; Muller, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 694 and references therein.

(23) von Schnering, H. G. *Bol. Soc. Quim.* **1988**, *33*, 41.

(24) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383.

(25) Lii, K.-H.; Haushalter, R. C. *J. Solid State Chem.* **1987**, *67*, 374.

(26) Cordier, G.; Ochman, H.; Schäfer, H. *J. Less Common Met.* **1986**, *119*, 291-296.

(27) Cordier, G.; Ochman, H.; Schäfer, H. *Rev. Chim. Miner.* **1985**, *22*, 58-63.

(28) Cordier, G.; Ochman, H.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1984**, *517*, 118.

(29) Cordier, G.; Ochman, H.; Schäfer, H. *Rev. Chim. Miner.* **1984**, *12*, 282-291.

0020-1669/90/1329-3892$02.50/0