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On the chemical transport of gallium oxide in the Ga_2O_3/H–Cl system

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Chemical tranpsort of gallium oxide using the H–Cl mixtures as transporting agents in a closed tube are investigated. No significant rate of crystal growth in the presence of stoichiometric HCl has been observed. Violent crystal growth was found for excess of chlorine as well as for the excess of hydrogen in the H–Cl system. For stoichiometric HCl and for the systems with excess of chlorine the crystals obtained appeared to be colourless while they were blue coloured for excess hydrogen. The experimental results are explained by the thermochemical calculations presented.

1. Introduction

The most stable structural modification of gallium oxide is monoclinic β-Ga_2O_3 [1, 2]. Gallium oxide dissociates at high temperatures [3, 4] and it is reported to exist as a partly reduced solid in the narrow range of Ga_2O_3–$Ga_2O_{2.992}$ [5].

Crystals of β-Ga_2O_3 were obtained by chemical vapour transport using I_2/S [6], $TeCl_4$ [7], iodine and Ga_2O [8] and chlorine [9] as transporting agents. Matsumoto *et al.* [10] obtained γ-Ga_2O_3 platelets as a result of reaction in the open system $Ga/HCl/O_2/Ar$. Sometimes the crystals obtained from the vapour phase proved to be non-stoichiometric coloured blue [8].

The composition of the vapour phase in the chemical vapour transport (CVT) processes for the $Ga_2O_3/TeCl_4$ [7] and Ga_2O_3/Cl_2 [9] systems was analysed by means of thermodynamic calculations and the $GaCl_3$ and $GaCl_2$ clorides were reported to be predominant. On the other hand, from spectroscopic investigations as well as from thermodynamic calculations, it appears that in the vapour phase of Ga–V–H–Cl systems (where V = nitrogen, phosphorus, arsenic, antimony), either GaCl or $GaCl_3$, depending on temperature and chlorine pressure, may be the most popular form of gallium chlorides [11, 12].

The aim of the present paper is to study the chemical transport and crystal growth of gallium oxide in the Ga_2O_3/H–Cl systems.

2. Thermodynamic considerations

On the basis of thermodynamic calculations the composition of the vapour phase in the Ga_2O_3/H–Cl systems has been determined for several, different values of the H/Cl ratio at total pressure $\Sigma P = 2$ atm. It has been assumed that the vapour phase of the system may consist of different gallium chlorides, other volatile gallium compounds (as GaO, Ga_2O, Ga, GaOH) and the other products of the reactions of Ga_2O_3 with Cl_2 (O_2, O, ClO, Cl_2O, Cl) as well as volatile products of the etching of silica wall (SiO, $SiHCl_3$, $SiCl_4$, SiH_4).

Although many authors either investigated the chemical transport processes of Ga–V (V = nitrogen, phosphorus, arsenic, antimony) compounds and their solid solutions or they determined the equilibrium constants for particular reactions of gallium chlorides with different agents, yet thermochemical data of some gallium chlorides seem to be controversial [9]. Thus, all the thermochemical data on gallium compounds used in the presented calculations are listed in Tables I and II. The other data are taken from [13].

From calculations it appears that the GaCl molecule is the main form of gallium chlorides abounding

TABLE I Data used in thermodynamic analysis

Substance	ΔH^0_{298} (kcal mol^{-1})	S^0_{298} (cal mol^{-1} K)	$C_p = a + (b \times 10^{-3})T + (c \times 10^5)T^{-2}$ (cal mol^{-1} K)			Reference
			a	$b(10^3)$	$c(10^{-5})$	
$Ga_2O_{3(s)}$	-260.3	20.31	26.98	3.69	-5.02	[13]
$GaCl_{(g)}$	-19.54	57.36	9.082	0	-0.481	[13]
$GaCl^a_{3(g)}$	-106.281	69.39	20.66			[13, 14]
$GaCl^b_{3(g)}$	-109.421	76.494	15.242	1.42	-0.081	[13,15]
$GaOH_{(g)}$	-35.37	59.27				[16]
$Ga_2O_{(g)}$	-20.5	67.8				[3]
$GaO_{(g)}$	33.747	55.17				[3]
$Ga_{(g)}$	65.235	40.375				[3]
$Ga_{2(g)}$	97.748	61.6				[3]

[a] Evaluated from the log *K*(T) for the reaction $GaCl_{3(l)} = GaCl_{3(g)}$ in [9].
[b] Evaluated from the log *K*(T) for the reaction $GaCl_3 + H_2 = GaCl + 2HCl$ in [9] ($cal_{th} = 4.184$ J).

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TABLE II Equilibrium constants of reactions used in thermodynamic analysis

Reaction	$-RT \ln T = \Delta G^0 (\mathrm{cal\,mol^{-1}})$	Temperature range (K)	Reference
$Ga_2Cl_6 = 2GaCl_3$	$21.024 \times 10^3 - 32.33T$	570 to 790	[17]
$Ga_2Cl_4 = GaCl + GaCl_3$	$23.3376 \times 10^3 - 28.8288T$	730 to 1070	[18]
$2GaCl = Ga_2Cl_2$	$-19.9949 \times 10^3 + 30.0148T$		[19]
$2GaCl_2 = Ga_2Cl_4^a$	$-20.49824 \times 10^3 + 31.17144T$		a

aInterpolation of values of log K(T) for the reactions $Ga_2Cl_6 = 2GaCl_3$ [17] and $2GaCl = Ga_2Cl_2$ [19] ($\mathrm{cal_{th}} = 4.184\,J$).

in the $Ga_2O_3/H{-}Cl$ systems while the $GaCl_3$ chloride is the predominant one if the value of the H : Cl rate approximates 1 or if it is even less (Figs 1 and 2). In such case the errors of thermodynamic data of $GaCl_3$ prove to influence the solution and thermodynamic analysis of the CVT process. If the data reported by Komshilova *et al.* [14] for $GaCl_3$ are extrapolated up to 1500 K, then the balance pressure of gallium p^*_{Ga} increases slightly with temperature and hot zone – cool zone direction of Ga_2O_3 transport can be expected for H/Cl = 1. However, when Kirwan's data [15] are used in the same calculations, then the reverse, cool zone – hot zone directions of transport may be supposed as the values of p^*_{Ga} decreases with temperature (Fig. 3).

From calculations it appears also that the value of p^*_{Ga} depends on temperature more strongly if the H/Cl ratio differs from one (Fig. 4). The excess of hydrogen may lead to significant decreases in the partial pressure of oxygen (Fig. 5) accompanied by the increase in the GaOH pressure. These conclusions are true in the case of the Komshilova's data [14] as well as the Kirwan's [15] data although the results presented in the figures concern only the calcuations performed for the Komshilova's data.

3. Experimental details

The experiments were carried out in transparent ampoules. The inner diameter of an ampoule was 18 mm and the length was about 120 mm (volume ~ 30 cm^3). Gallium oxide of analytical grade purity, precalcinated in the air for 6 h at 1300 K was used in the experiments as the initial substance.

As transporting agents different mixtures of Cl_2 and H_2O were introduced together with exactly calculated amounts of gallium which tied the excess of oxygen and formed Ga_2O_3 according to the following reactions for H/Cl = 1 : 3

$$1.5H_2O + Ga + 4.5Cl_2 = 0.5Ga_2O_3 + 3HCl + 3Cl_2 \qquad (1)$$

for H/Cl = 1

$$3H_2O + 2Ga + 3Cl_2 = Ga_2O_3 + 6HCl \qquad (2)$$

for H/Cl = 3 : 1

$$1.5H_2O + Ga + 0.5Cl_2 = 0.5Ga_2O_3 + HCl + H_2 \qquad (3)$$

Liquid chlorine was introduced into an ampoule in a sealed glass capillary. Water was obtained by the thermal decomposition of $CuSO_4 \cdot 6H_2O$ under vacuum. Gallium of analytical grade purity was added together with Ga_2O_3.

Crystallization processes were investigated in the range of 800 to 1300 K and the amounts of transporting agents were changed so that the pressure of 2 to 4 atm was preserved. The crystals obtained in the chemical transport experiments and the rest of the source material were subjected to X-ray analysis.

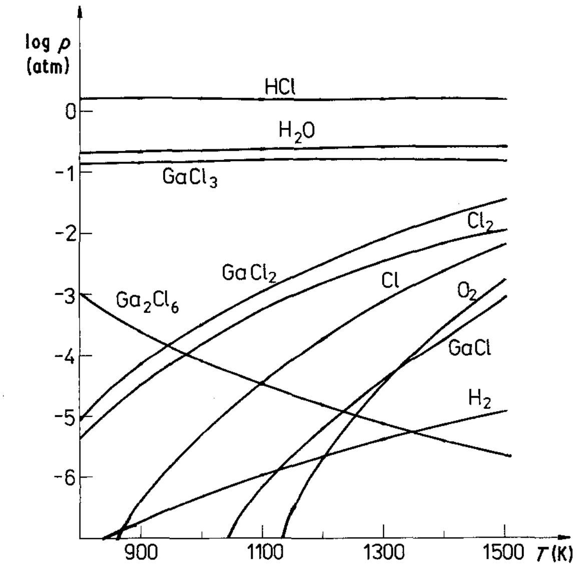

Figure 1 Equilibrium partial pressures p_i against temperature in the system Ga_2O_3/HCl at the total pressure $\Sigma P = 2$ atm (1 atm = 1.013×10^5 Pa).

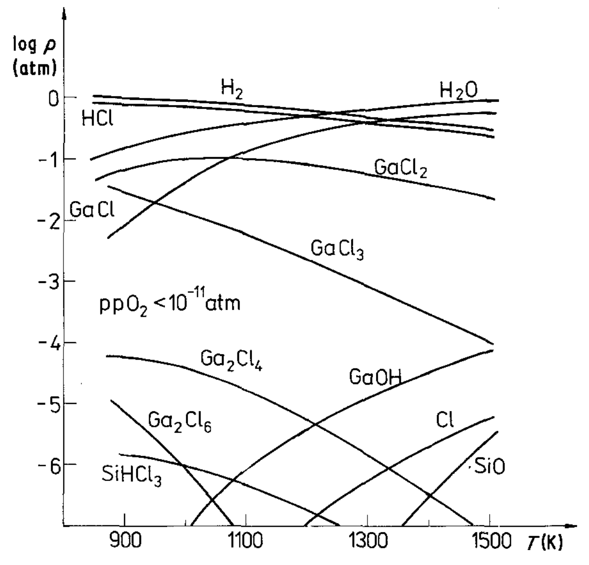

Figure 2 Equilibrium partial pressures p_i against temperature in the $Ga_2O_3/H{-}Cl$ system, where the ratio H/Cl = 3 at the total pressure $\Sigma P = 2$ atm (1 atm = 1.013×10^5 Pa).

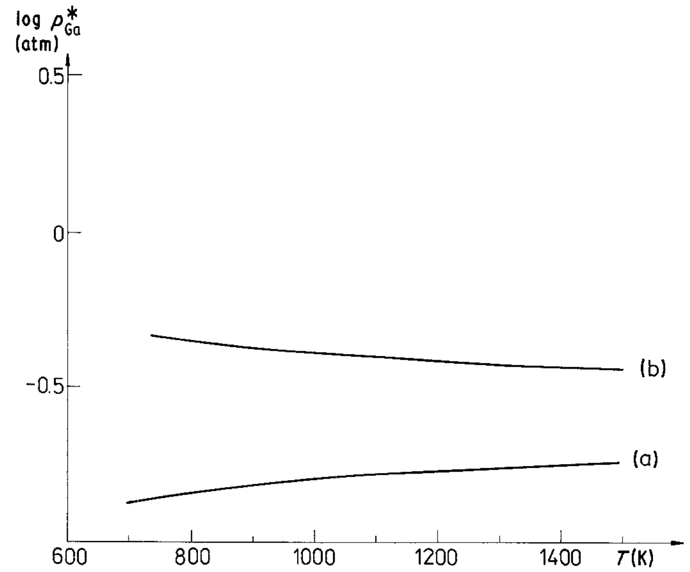

Figure 3 Balance pressure p^*_{Ga} in the Ga_2O_3/HCl system against temperature; the results for (a) Komshilova's *et al.* [14] and (b) Kirwin's [15] data are compared at the total pressure ΣP = 2 atm (1 atm = 1.013 × 10^5 Pa).

4. Results and discussion

Until 1200 K no process of Ga_2O_3 transport with HCl was observed. Above 1200 K Ga_2O_3 proved to be transported by HCl and the hot zone – cool zone direction of transport as well as the cool zone – hot zone one occurred. In both the cases colourless small crystals were found along the whole inside wall of the ampoules. The process can be explained by small changes of the balance pressure of gallium p^*_{Ga} against temperature in the HCl system (Figs 3 and 4). Above 1300 K the process of etching of the quartz wall was observed. The lattice parameters of the obtained crystals correspond to the literature data [2] well.

The experiments carried out in the same temperature conditions for the following H/Cl ratios: 9.0, 3.0, 1.2 and 0.33, proved that only the hot zone – cool zone direction of transport is possible in the systems. Only crystals obtained at the H/Cl ratio = 9 reacted with the quartz ampoule (Fig. 6d). The rate of transport increased significantly for the H/Cl $\neq$ 1 systems. The results of some experiments for the crystallization temperature 1000 K, ΔT = 50 K and ΣP = 2 atm are presented in Table III.

All the results confirm the presented thermodynamic analysis i.e. that p^*_{Ga} as a function of temperature seems to be almost constant for the Ga_2O_3/HCl system and the value of dp^*_{Ga}/dT seems to increase for the H/Cl $\neq$ 1 systems. The rate of transport increases with excess hydrogen in the system and the supersaturation of gallium gaseous compounds is responsible for the chemical vapour transport of Ga_2O_3 in the reducing as well as oxidizing atmosphere. Crystals obtained in the processes with the hydrogen as well as chlorine excess are presented in Fig. 6a to d. The crystals appeared to be blue coloured if the H/Cl ratio was higher than 1 (Figs 6b to d). However, X-ray diffraction analysis shows the monoclinic β-Ga_2O_3 structure of the products of all investigated processes.

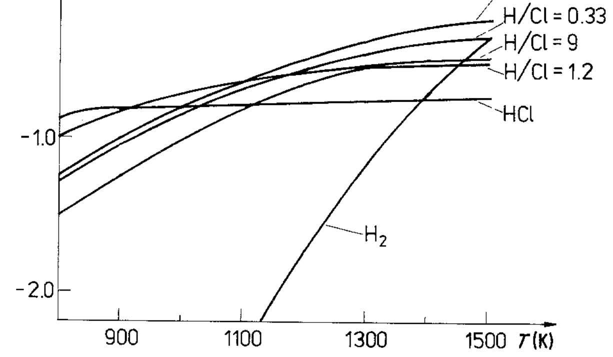

Figure 4 Balance pressure p^*_{Ga} against temperature for the various ratios H/Cl and for H_2 at the total pressure ΣP = 2 atm (1 atm = 1.013 × 10^5 Pa).

Matsumoto *et al.* [10] and Lorenz *et al.* [8] concluded that the blue coloured crystals of β-Ga_2O_3 are non-stoichiometric. This is confirmed by the thermodynamic calculations presented in Fig. 5, as the equilibrium partial pressure of oxygen in the Ga_2O_3/H–Cl systems, for the H/Cl = 1.2, 3 and 9 ratios, proves to be lower than the decomposition partial pressure of oxygen over solid stoichiometric Ga_2O_3.

5. Summary

This work deals with the problem of chemical vapour transport in closed Ga_2O_3/H–Cl systems (on the basis of thermodynamic considerations as well as experiments). Experimental results proved that the rate of transport is very low for the stoichiometric HCl and it increases apparently if either a hydrogen or chlorine mixture is used.

From thermodynamic calculations it appears that the equilibrium phase of the Ga_2O_3/HCl system is almost constant as a function of temperature and it

TABLE III The rate of mass transport of gallium oxide for various H/Cl ratios, the hot zone – 1050 K, the cool zone – 1000 K and $\Sigma P \cong$ 2 atm (1 atm = 1.013 × 10^5 Pa)

H/Cl ratio	Transport rate [mg h^{-1}]
0.33	7.5
1.2	3.3
3.0	more than 11.25
9.0	more than 12.5

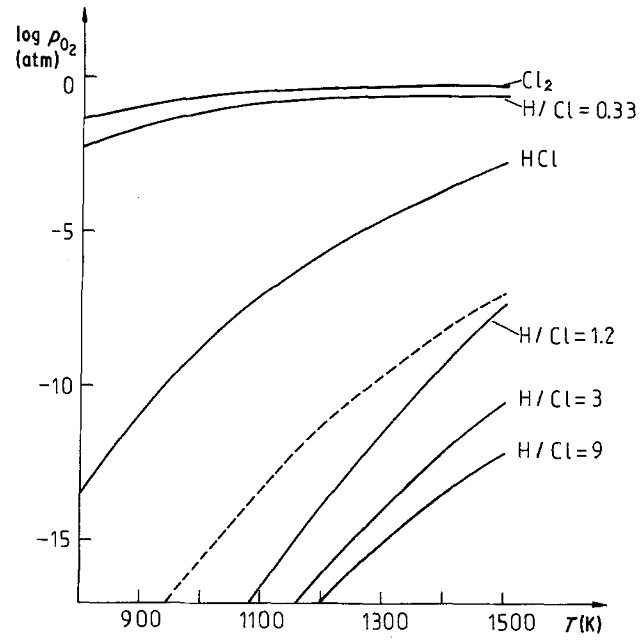

Figure 5 Partial pressure pO_2 against temperature for the various ratios H/Cl and for Cl_2 at the total pressure $\Sigma P = 2$ atm, (- -) decomposition partial pressure of oxygen over Ga_2O_3 according to Piekarczyk and Pajaczkowska [3] (1 atm = 1.013×10^5 Pa).

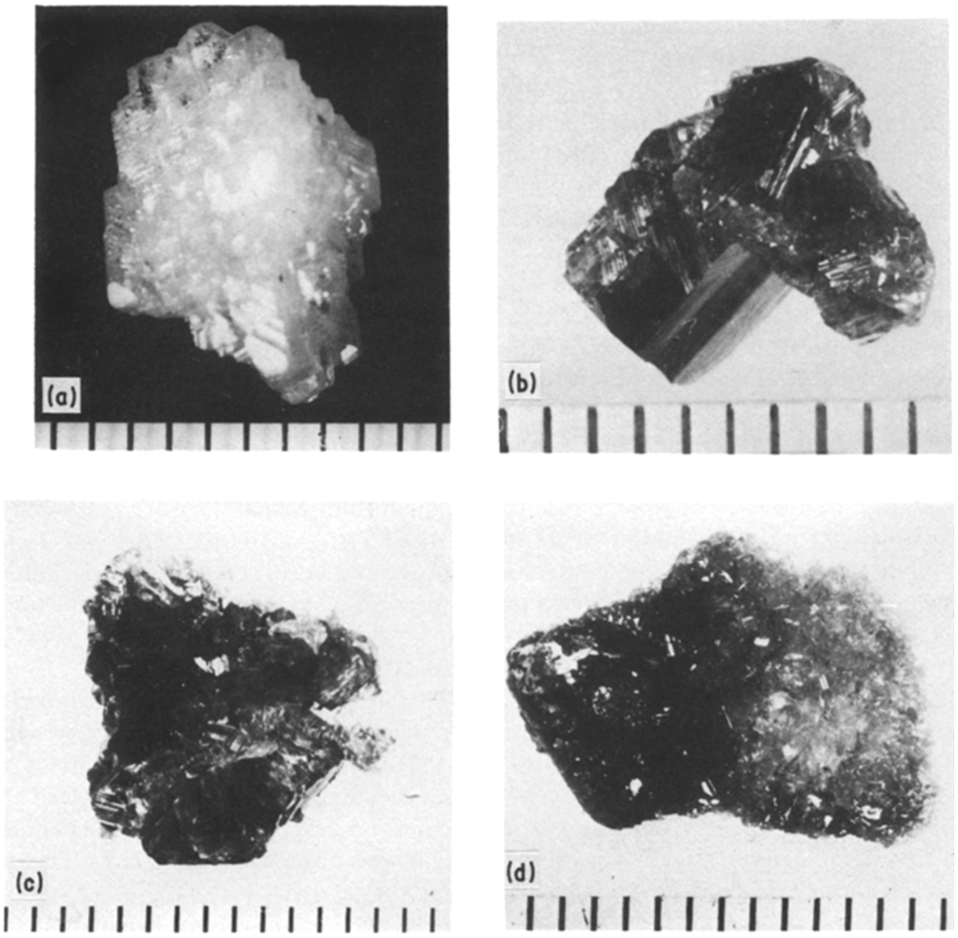

Figure 6 β-Ga_2O_3 crystals grown in the H–Cl systems for the following H/Cl ratios: (a) 0.33; (b) 1.2; (c) 3; (d) 9 at the temperature 1300 to 1250 K and $\Sigma P = 2$ atm (1 atm = 1.013×10^5 Pa) scale in mm.

depends on temperature much stronger if the excess of one of the components is introduced.

The crystals obtained proved to be colourless if the stoichiometric HCl or any other mixture with chlorine was used as a transporting agent and if excess hydrogen was used then blue coloured crystals were obtained. These facts are connected with the stoichiometry of the crystals. Further calculations showed that in the latter systems the value of equilibrium partial pressure of oxygen is lower than the value of decomposition pressure of oxygen over solid, stoichiometric Ga_2O_3.

References

1. R. ROY, V. G. HILL and E. F. OSBORN, *J. Amer. Ceram. Soc.* **74** (1952) 719.

2. S. GELLER, *J. Chem. Phys.* **33** (1960) 676.
3. W. PIEKARCZYK and A. PAJACZKOWSA, *J. Cryst. Growth* **46** (1979) 483.
4. M. SAURAT and A. REVCOLEVSCHI, *Rev. Int. Hautes Temper. Refract.* **8** (1971) 291.
5. S. A. SHTSHUKAREV, G. A. SEMENOV and I. A. RAT'KOVSKIJ, *Zh. Neorg. Khim.* **14** (1969) 3.
6. R. NITSCHE, *J. Phys. Chem. Solids, Suppl.* **1** (1967) 215.
7. M. GERLACH and H. OPPERMANN, *Z. anorg. allg. Chem.* **432** (1977) 17.
8. M. R. LORENZ, J. F. WOODS and R. J. GAMBINO, *J. Phys. Chem. Solids* **28** (1967) 403.
9. H. JUSKOWIAK and A. PAJACZKOWSKA, *ibid.* in press.
10. T. MATSUMOTO, M. AOKI, KINOSHITA and T. AONO, *Jpn. J. Appl. Phys.* **13** (1974) 1578.
11. M. A. ZEUGEL, *J. Electrochem. Soc.* **112** (1965) 1153.
12. V. S. BAN, *J. Cryst. Growth* **17** (1972) 19.
13. I. BARIN, O. KNACKE and O. KUBASCHEWSKI, in "Thermochemical Properties of Inorganic Substances, Supplement" (Springer-Verlag, Berlin, 1977).
14. O. N. KOMSHILOVA, O. G. POLAYCHENOK and G. I. NOVIKOV, *Zh. Neorg. Chim.* **15** (1970) 251.
15. D. J. KIRWAN, *J. Electrochem. Soc., Sol. State Sc.* **117** (1970) 1572.
16. D. BATTAT, M. M. FAKTOR, J. GARRET and R. H. MOSS, *J. Chem. Soc. Faraday Trans. I* **70** (1974) 2280.
17. W. FISHER and O. JUBERMANN, *Z. anorg. allg. Chem.* **227** (1936) 227.
18. Y. KUNIYA and M. HOSAKA, *J. Cryst. Growth* **28** (1975) 385.
19. O. G. POLAYACHENOK and O. N. KOMSHILOVA, *Zh. Fiz. Khim.* **45** (1971) 990.

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