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Chemical transport of β-Ga_2O_3 using chlorine as a transporting agent

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The chemical transport of Ga_2O_3 with chlorine as a transporting agent has been investigated. Thermochemical properties of gallium chlorides have been considered on the basis of literature data. Thermodynamic analysis of transport reactions at 600 to 1500 K has been performed and $GaCl_3$ was found the predominant gallium chloride in the vapour phase. The crystallization temperature of about 1150 to 1250 K proved to be the best conditions for the crystal growth of β-Ga_2O_3.

1. Introduction

Gallium oxide melts at about 2000 K [1–3] and it is known to dissociate at high temperature [4]. It may occur in five structural modifications: α, β, γ, δ and ε [5]. The most stable is β-Ga_2O_3 and its monoclinic structure was investigated in detail by Geller [6]. Single crystals of β-Ga_2O_3 were obtained by the Verneuil technique [2, 7], by the floating zone method [7], from high temperature solution [7–10] and from the vapour phase. Such transporting agents as I_2/S [11], $TeCl_4$ [12] iodine and Ga_2O [13] were reported. Matsumoto *et al.* [14] obtained β-Ga_2O_3 platelets as a result of reaction in the $Ga/HCl/O_2/Ar$ system. Sometimes crystals obtained from the vapour phase proved to be non-stoichiometric (blue-coloured) [13].

The purpose of the present paper is to study the chemical transport of Ga_2O_3 with Cl_2 on the basis of experiments as well as thermochemical calculations of the equilibrium composition.

2. Thermochemical considerations

Many authors either investigated Ga–Cl [15–24] and Ga–HCl [24–29] systems or determined the equilibrium constants of some particular reactions of gallium chlorides with different agents [22, 23]. The Ga–Cl system was also discussed by Chatillon and Bernard [30]. However, all the results do not correspond well with one another and they lead to serious differences in the evaluated values of Gibbs free energy, $\Delta G_f^0(T)$, for gaseous $GaCl_3$ (Fig. 1).

According to the available data [18, 20–23, 31], in more detailed analysis of the Ga_2O_3/Cl_2 system it seems sensible to use differently expressed thermochemical data for gaseous $GaCl_3$ i.e. Komshilova's data [31] in the range of low temperature and Kirwan's data [23] in the range of high temperature (Fig. 1).

As gallium oxide is known to dissociate at high temperature, the vapour phase of the Ga_2O_3/Cl_2 system is also suspected of containing a certain amount of the products of such a process. Initial analysis, based on the same data that Piekarczyk and Pajaczkowska [4] had used, is presented in Table I. It appears that the partial pressures of the products compared to the partial pressure of oxygen are supposed to be very low and may be neglected below 1000 K.

Thus, it has been assumed that the Ga_2O_3/Cl_2 system consists of two phases i.e. solid Ga_2O_3 and the vapour phase which may contain three groups of species:

1. volatile gallium chlorides-monomers as well as dimers;
2. different products of thermal dissociation of Ga_2O_3 above 1000 K;
3. the other products of reaction Cl_2 with Ga_2O_3.

The calculations of equilibrium state composition have been performed in the range of 0.2 to 4 atm of the total pressure for the temperature range of 600 to 1500 K.

The data used in calculations [15, 17, 21, 23, 30–32] are listed in Tables II and III and the results are shown in Figs 2 and 3.

TABLE I Pressure of the products of thermal dissociation of Ga_2O_3 expressed by the pressure of oxygen*

Substance	$\log p_{(i)}$ [atm] $= f(T)$ [K]		
(i)	500 K	1000 K	1500 K
$Ga_2O_{(g)}$	$-83.7 - \log p_{O_2}$	$-31.3 - \log p_{O_2}$	$-13.85 - \log p_{O_2}$
$GaO_{(g)}$	$-60.7 - 1/4 \log p_{O_2}$	$-24.88 - 1/4 \log p_{O_2}$	$-12.94 - 1/4 \log p_{O_2}$
$Ga_{(g)}$	$-62.88 - 3/4 \log p_{O_2}$	$-28.07 - 3/4 \log p_{O_2}$	$-13.83 - 3/4 \log p_{O_2}$
$Ga_{2(g)}$	$-131.5 - 3/2 \log p_{O_2}$	$-53.27 - 3/2 \log p_{O_2}$	$-27.19 - 3/2 \log p_{O_2}$
$O_{(g)}$	$-23.0 + 1/2 \log p_{O_2}$	$-9.96 + 1/2 \log p_{O_2}$	$-5.62 + 1/2 \log p_{O_2}$

*Calculated from the thermochemical data cited in [4].

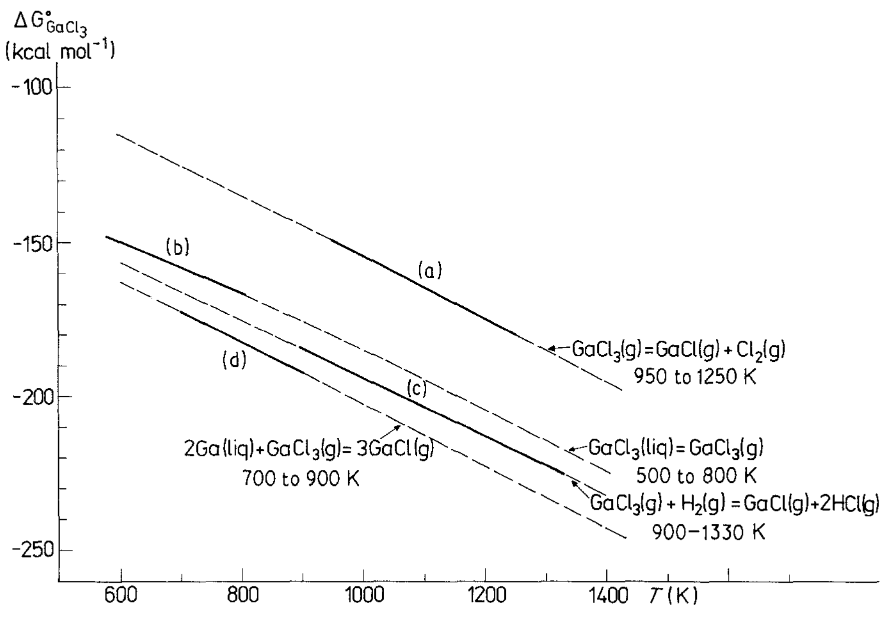

Figure 1 Thermochemical properties of gaseous $GaCl_{3(g)}$. Gibbs free energy $\Delta G^0_{GaCl_3}$ as a function of temperature (T) is evaluated from the equilibrium constants of different reactions according to: (a) Kuniya [20, 21]; (b) Komshilova *et al.* [31]; (c) Kirwan [23] using the thermochemical data listed by Barin *et al.* [32].

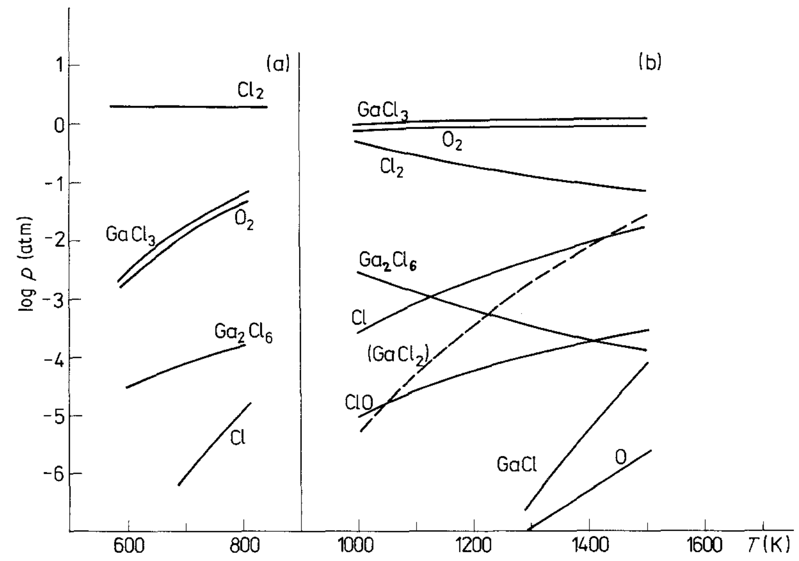

Figure 2 Equilibrium partial pressures as a function of temperature in the system $Ga_2O_3 : Cl_2$ for the low temperature range (a) Komshilova's *et al.* data [31] for $GaCl_3$ have been used and for the high temperature range (b) Kirwan's data [23].

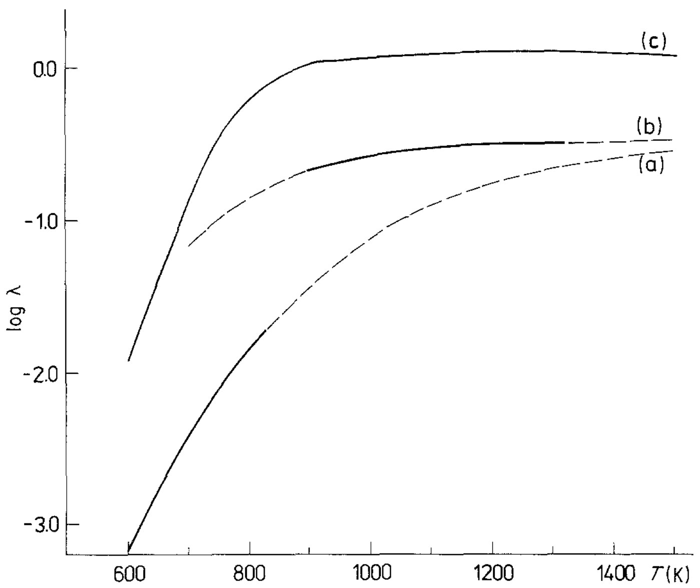

Figure 3 Equilibrium solubility of gallium against temperature for $\Sigma P = 2\,atm$ in the vapour phase of $Ga_2O_3 : Cl_2$ system $\lambda = p^x_{Ga}/p^x_{Cl}$ when (a) Komshilova's *et al.* [31] (b) Kirwan's [23] and (c) Chatillon and Bernard's [30] data are used in calculations.

TABLE II Data used in thermodynamic analysis

Substance	ΔH^0_{298} (kcal mol^{-1})	S^0_{298} (cal mol^{-1} K)	$C_p = a + b\,10^{-3}T + c\,10^5 T^{-5}$ (cal mol^{-1} K)			Reference
			a	$b(10^3)$	$c(10^{-5})$	
$Ga_2O_{3(s)}$	−260.2	20.31	26.98	3.69	−5.02	[32]
$GaCl_{(g)}$	−19.54	57.36	9.082	0	−0.481	[32]
$O_{2(g)}$	0	49.005	7.16	1.0	−0.4	[32]
$Cl_{2(g)}$	0	55.3	8.82	0.06	−0.68	[32]
$Cl_{(g)}$	28.988	39.453	5.505	−0.179	−0.166	[32]
$ClO_{(g)}$	24.19	54.145	8.585	0.293	−1.055	[32]
$Cl_2O_{(g)}$	21.0	64.019	13.573	0.175	−2.005	[32]
$Ga_2O_{(g)}$	−20.5	67.8				[4]
$GaO_{(g)}$	33.747	55.17				[4]
$Ga_{(b)}$	65.235	40.375				[4]
$Ga_{2(g)}$	97.748	61.6				[4]
$O_{(g)}$	59.556	38.467				[4]
$GaCl_{3(g)}$*	−106.281	69.39	20.66			[32, 31]
$GaCl_{3(g)}$†	−109.421	76.494	15.242	1.42	−0.81	[23, 32]

*Evaluated from the log $K(T)$ for the reaction $GaCl_{3(l)} = GaCl_{3(g)}$ (Fig. 1b).

†Evaluation from the log $K(T)$ for the reaction $GaCl_3 + H_2 = GaCl + 2HCl$ (Fig. 1c).

From the calculations it appears that the value of gallium solubility in vapour phase of the Ga_2O_3/Cl_2 system is determined by the value of the partial pressure of $GaCl_3$ and, as a consequence, no doubt the accuracy of the $GaCl_3$ thermodynamical data would be most important in any detailed investigations of Ga_2O_3 transport while the errors of thermodynamic data of the other gallium compounds would not influence such analysis (Figs 2 and 3).

Partial pressures of all the dissociation products of Ga_2O_3 are negligible even at high temperature.

For the whole range of temperatures 600 to 1500 K only the hot zone–cool zone direction of Ga_2O_3 transport is supposed to occur (Figs 2 and 3).

Some additional calculations have been performed for the Ga_2O_3–SiO_2/Cl_2 and Ga_2O_3/Cl_2–H_2O systems. It appears that in the Ga_2O_3–SiO_2/Cl_2 system the equilibrium partial pressure of the most volatile of the products of the etching of silica ampoules i.e. gaseous $SiCl_4$, reaches only 10^{-10} atm at 1000 K and 10^{-7} atm at 1500 K while the total pressure is 2 atm.

It also appears from further calculations that the value of transport rate in the Ga_2O_3/Cl_2 system may be sensitive to such small amounts of H_2O as the one expressed by the molar ratio $H_2O/Cl_2 = 0.005$.

3. Experimental details

The experiments were carried out in ampoules of transparent quartz glass with an inner diameter of 18 mm and length of about 120 mm, the volume of the ampoule was about 30 cm^3. The ampoules were previously annealed in air at 1400 K. The initial substance used in the experiments was Ga_2O_3 of analytical grade purity. Gallium oxide was precalcinated in air for 6 h at 1300 K. Calculated amount of liquid chlorine was introduced into an ampoule in a sealed glass capillary. Additionally, in order to eliminate the traces of water, the ampoule with Ga_2O_3 was annealed under vacuum up to 450 K. The crystallization processes were investigated in the temperature range 500 to 1300 K and the amount of chlorine was changed from 0.5 to 4 mg cm^{-3}. Sealed ampoules were kept for 1 day under a reverse temperature gradient. The crystal growth was allowed to proceed for 3 to 6 days. After the chemical transport experiments the crystals were subjected to X-ray structure analysis.

4. Results and discussion

Chlorine proved to be an effective transporting agent for Ga_2O_3. Some of the obtained crystals are shown in Fig. 4. All the crystals are colourless. X-ray analysis shows a monoclinic structures for the obtained crystals as well as the substance which remained in the source zone. The lattice parameters correspond well to the literature data β-Ga_2O_3 [6].

The investigations of chemical transport of Ga_2O_3 have shows that below 900 K only traces of Ga_2O_3 have been found in the crystallization zone for the wide range of temperature difference between the zones (20 to 150 K) and total pressure.

Above 900 K the experimental rate of transport increases violently. The results of the experiments performed for two ranges of temperature 1220 to 1170 K and different amount of transporting agent chlorine are presented in Fig. 5. Direction of the transport always agrees with prediction, i.e. Ga_2O_3 is transported from the hot zone to the cool one and the cool–hot zone transport of Ga_2O_3 has not been found.

TABLE III Data used in thermodynamic analysis

Reaction (g)	$-RT\ln(T) = \Delta G^0$ (cal mol^{-1})	Temperature range (K)	Reference
$Ga_2Cl_6 = 2GaCl_3$	$21.024 \times 10^3 - 32.33T$	570 to 790	[15]
$Ga_2Cl_4 = GaCl + GaCl_3$	$23.3376 \times 10^3 - 28.8288T$	730 to 1070	[21]
$2GaCl = Ga_2Cl_2$	$-19.9949 \times 10^3 + 30.0148T$		[17]
$2GaCl_2 = Ga_2Cl_4$*	$-20.49824 \times 10^3 + 31.17144T$		*

*Interpolation of values of log $K(T)$ for the reactions $Ga_2Cl_6 = 2GaCl_3$ [15] and $2GaCl = Ga_2Cl_2$ [17].

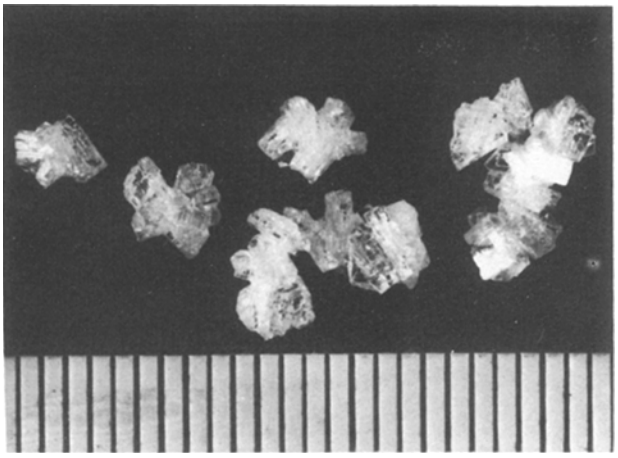

Figure 4 β-Ga_2O_3 crystals grown by chemical vapour transport with chlorine (scale in mm).

Above 1300 K, the temperature of the chemical vapour transport (CVT) process is limited by intensive reactivity between Ga_2O_3 and the quartz ampoule.

The crystallization temperature of about 1150 to 1250 K and the temperature difference of about 30 to 70 K proved to be the best conditions for the crystal growth of β-Ga_2O_3 in the Ga_2O_3/Cl_2 system.

As it appears from temperature dependence dp^*_{Ga}/dT (Fig. 6) below 900 K significant values of transport rate will be expected if the extrapolated Kirwan's data [23] for gaseous $GaCl_3$ are used in thermochemical calculations. Thus, the experimental results confirm that Kirwan's data should not be extrapolated to the range of 600 to 900 K and suggest that the solubility of Ga_2O_3 in the vapour phase is very low at low temperature. For the same reasons thermochemical data tabulated by Chatillon and Bernard [30] seems not to be confirmed by the temperature dependence of the experimental rate of transport (Figs 3 and 6).

5. Summary

In the paper the chemical transport of Ga_2O_3 with chlorine is studied on the basis of experiments as well as thermochemical calculations of the equilibrium composition.

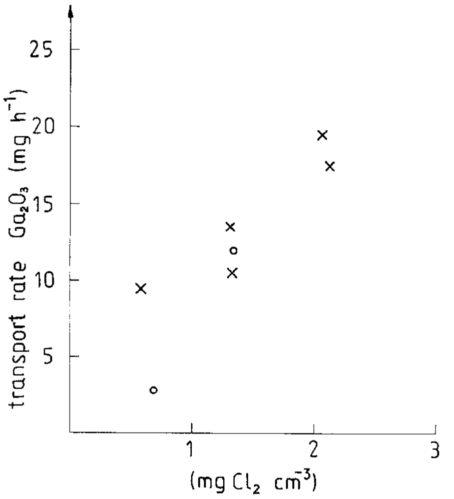

Figure 5 The rate of transport in the Ga_2O_3/Cl_2 system – some experimental results performed for 1220 to 1170 K (×) and 1170 to 1140 K (o) and for various amounts of transporting agent chlorine.

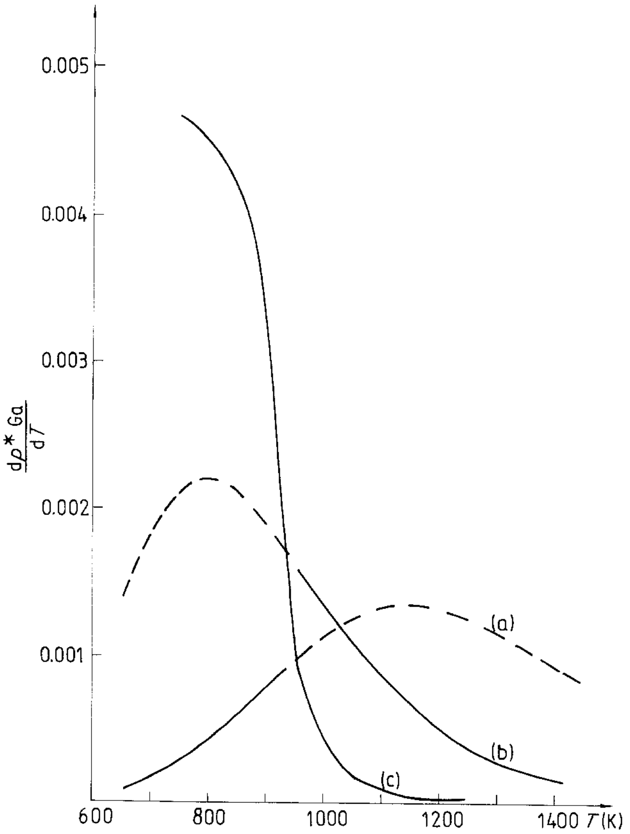

Figure 6 Derivative dp^*_{Ga}/dT calculated for the equilibrium state in the $Ga_2O_3 : Cl_2$ system for $\Sigma P = 2$ atm calculated as a function of temperature when (a) Komshilova's *et al* [31], (b) Kirwan's [23] and (c) Chatillon and Bernard's [30], data are used; p^* Ga is known as balance pressure of Ga.

Thermochemical properties of gallium chlorides were considered on the basis of literature data. From the calculations, performed for the range of 600 to 1500 K, it appeared than in the Ga_2O_3 system:

1. The value of gallium solubility in the vapour phase is determined by the value of the partial pressure of $GaCl_3$ and the accuracy of the $GaCl_3$ thermochemical data is most important in any detailed investigations of the Ga_2O_3 transport.
2. Only the hot–cool zone direction of transport is supposed to occur.
3. At 1500 K the equilibrium partial pressure of the most volatile of the products of etching of quartz ampoule reaches about 10^{-7} atm.
4. The rate of transport may be sensitive to even a very small amount of H_2O.

Experiments were carried out in the range of 500 to 1300 K using different amounts of chlorine. The traces of water were previously removed out of the experimental ampoules. It appeared that:

1. Direction of transport agrees with prediction.
2. The crystals obtained in the CVT processes with chlorine as a transporting agent are colourless β-Ga_2O_3.
3. Below 900 K only traces of Ga_2O_3 are transported and this fact seems not to confirm the data tabulated by Chatillon and Bernard [30] (Figs 3 and 6).

References

1. V. G. HILL, R. ROY and E. F. OSBORN, *J. Amer. Ceram. Soc.* **35** (1952) 135.
2. A. B. CHASE, *ibid.* **47** (1964) 470.
3. I. BARIN and O. KNACKE, in "Thermochemical Properties of Inorganic Substances" (Springer-Verlag, Berlin, 1973).
4. W. PIEKARCZYK and A. PAJACZKOWSKA, *J. Cryst. Growth* **46** (1979) 483.
5. R. ROY, W. G. HILL and E. F. OSBORN, *J. Amer. Ceram. Soc.* **74** (1952) 719.
6. S. GELLER, *J. Chem. Phys.* **33** (1960) 676.
7. M. SAURAT and A. REVCOLEVSCHI, *Rev. Int. Hautes Temper. Refract.* **8** (1971) 291.
8. G. KATZ and R. ROY, *J. Amer. Cram. Soc.* **49** (1966) 168.
9. G. GARTON, S. H. SMITH and B. M. WANKLYN, *J. Cryst. Growth* **13/14** (1972) 588.
10. V. I. VORONKOVA, V. K. IANOWSKII and V. A. KOPCUK, *Ukr. Fiz. Zh.* **28** (1983) 36.
11. R. NITSCHE, *J. Phys. Chem. Solids, Suppl.* **1** (1967) 215.
12. M. GERLACH and H. OPPERMANN, *Z. anorg. allg. Chem.* **432** (1977) 17.
13. M. R. LORENZ, J. F. WOODS and R. J. GAMBINO, *J. Phys. Chem. Solids* **28** (1967) 403.
14. T. MATSUMOTO, M. AOKI, A. KINOSHITA and T. AONO, *Jpn. J. Appl. Phys.* **13** (1974) 1578.
15. W. FISHER and O. JUBERMANN, *Z. anorg. allg. Chem.* **227** (1936) 227.
16. A. W. LAUBENGAYER and F. B. SCHRIMER, *J. Amer. Chem. Soc.* **62** (1940) 1578.
17. O. G. POLYACHENOK and O. N. KOMSHILOVA, *Zh. Fiz. Khim.* **45** (1971) 990.
18. H. SCHAFER and M. BINNEWIES, *Z. anorg. allg. Chem.* **410** (1974) 251.
19. *Idem, Rev. Chim. Miner.* **13** (1976) 24.
20. Y. KUNIYA, M. HOSAKA and I. SHINDO, *Denki Kagaku Oyobi Kogyo Butsuri Kagaku* **43** (1975) 372.
21. Y. KUNIYA and M. HOSAKA, *J. Cryst. Growth.* **28** (1975) 385.
22. M. A. ZEUGEL, *J. Electrochem. Soc.* **112** (1965) 1153.
23. D. J. KIRWAN, *ibid.* **117** (1970) 1572.
24. D. BATTAT, M. M. FAKTOR, J. GARETT and R. H. MOSS, *JCS Faraday Trans. I* 7 (1974) 2302.
25. V. S. BAN, *J. Electrochem. Soc.* **118** (1971) 1473.
26. L. C. LUTHER and D. D. ROCCASECCA, *ibid.* **115** (1968) 815.
27. H. SEKI, *Jpn. J. Appl. Phys.* **7** (1968) 1324.
28. R. R. FERGUSON and T. GABOR, *J. Electrochem. Soc.* **111** (1964) 585.
29. G. KNOBLOCH, E. BUTTER and V. MEIER, *J. Cryst. Growth* **66** (1984) 338.
30. C. CHATILLON and C. BERNARD, *J. Cryst. Growth* **71** (1985) 433.
31. O. N. KOMSHILOVA, O. G. POLAYCHENOK and G. I. NOVIKOV, *Zh. Neorg. Chim.* **15** (1970) 251.
32. I. BARIN, O. KNACKE and O. KUBASCHEWSKI, in "Thermochemical Properties of Inorganic Substances Supplement" (Springer-Verlag, Berlin, 1977).

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