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Removal of oxygen from electronic materials by vapor-phase  
processes

Witold Palosz<sup>1,\*</sup>

*NASA, Marshall Space Flight Center, Space Sciences Laboratory, ES75, Huntsville, Alabama 35812, USA*

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# Journal of Crystal Growth

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# Removal of oxygen from electronic materials by vapor-phase processes

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*NASA, Marshall Space Flight Center, Space Sciences Laboratory, ES75, Huntsville, Alabama 35812, USA*

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## Abstract

Thermochemical analyses of equilibrium partial pressures over oxides with and without the presence of the respective element condensed phase, and hydrogen, chalcogens, hydrogen chalcogenides, and graphite are presented. Theoretical calculations are supplemented with experimental results on the rate of decomposition and/or sublimation/vaporization of the oxides under dynamic vacuum, and on the rate of reaction with hydrogen, graphite, and chalcogens. Procedures of removal of a number of oxides under different conditions are discussed.

## 1. Introduction

Electronic compounds are usually synthesized from high-purity elements typically of 6N purity (99.9999% with respect to metal impurities). Such materials may still contain non-metal contaminants, predominantly oxygen at levels of 100 ppm or higher. Oxide impurities present in crystal growth systems may (i) affect electronic properties of the materials, (ii) increase sticking of the growing crystals to the walls of the container (formation of silicates) leading to detrimental strains in the material, (iii) form excess gas(es) in the system, and (iv) through inclusion may lead to deterioration of crystallographic perfection of the materials.

High-purity elements are typically obtained by zone refining. Oxides are usually present as insoluble particles, that on zone refining may be retrapped by the solidification interface. Moreover, oxidation of materials may occur during handling of the elements and compounds in air. Therefore, the removal of oxides may be a critical factor in crystal growth and other materials processing. Some material preparation procedures reported in the literature include annealing in hydrogen [1–3] or hydrogen chalcogenides [4, 5] atmospheres. In this work, we systematically analyze and discuss physical and thermochemical conditions, and limitations of removal of different oxides (oxygen) of elements important for electronic applications. Theoretical predictions based on thermochemical analysis were verified experimentally. We investigated removal of the metal oxides  $\text{Bi}_2\text{O}_3$ ,  $\text{CdO}$ ,  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{GeO}$ ,  $\text{GeO}_2$ ,  $\text{HgO}$ ,  $\text{In}_2\text{O}_3$ ,  $\text{MnO}$ ,

\* Fax: +1 205 544 8762; e-mail: witold.palosz@msfc.nasa.gov.

<sup>1</sup> Universities Space Research Association.

PbO, Sb<sub>2</sub>O<sub>3</sub>, SnO, SnO<sub>2</sub>, and ZnO, and non-metal oxides As<sub>2</sub>O<sub>3</sub>, SO<sub>2</sub>, SeO<sub>2</sub>, and TeO<sub>2</sub>. Finally, we discuss the techniques used for the removal of oxides including vacuum evaporation, reduction by hydrogen and carbon (graphite), and volatilization by chalcogens and hydrogen chalcogenides.

## 2. General considerations

### 2.1. Mass transport limitations

The removal of oxides can be accomplished either by a direct vaporization (for simplicity, the term 'vaporization' will be used for *vaporization* and for *sublimation* throughout this paper) under (dynamic) vacuum or by a chemical volatilization of the oxide(s) in a flow or sealed system (followed by a vacuum treatment if necessary). Different mass transport (removal) mechanisms may dominate. For low total pressures ( $P_t < 10^{-5}$ – $10^{-6}$  atm) the mean free path of the gaseous species is larger than the characteristic length of the flow system (the Knudsen number  $Kn > 1$ ) and *molecular flow* ensues. Then the flow rate  $r$  (in moles per unit time) can be expressed as

$$r = \frac{a_v PS}{\sqrt{2\pi MRT}} \quad (1)$$

(Hertz–Knudsen equation [6]) where  $P$  is the (equilibrium) pressure of the component,  $M$  its molecular weight,  $R$  is the gas constant,  $T$  the temperature,  $S$  the cross-sectional area of the ampoule, and  $a_v$  is the vaporization coefficient. For a system with  $S = 1.76 \text{ cm}^2$  (ampoule ID 15 mm) and no kinetic limitations for vaporization ( $a_v = 1$ ), the removal of 100 ppm of an oxide from 0.1 mol of a matrix material in 1 h (which corresponds to the flow rate of  $r = 10^{-5} \text{ mol/h}$ ) requires a vapor pressure of  $P \approx 10^{-8} \text{ atm}$ . In real systems the vaporization coefficient may be less than unity and higher pressures (i.e. temperatures) than those anticipated from Eq. (1) for  $a_v = 1$  may have to be applied. For flow in a tube, collisions of the molecules with the tube reduce the flow rate by a factor dependent on the tube's length-to-radius ratio [7]. This factor, calculated for our conditions ( $L/a = 10/0.75$ ), is 0.154.

When  $Kn < 0.01$  [8], the mass transport is controlled by *viscous flow*

$$V = \frac{\pi}{8} \frac{1}{\eta} \frac{\Delta P_t}{\Delta L} a^4 = \frac{\pi a^2 RT J}{P_t} \quad (2)$$

(Hagen–Poiseuille equation [6]) where  $V$  is the flow rate (in volume per unit time),  $\eta$  is the viscosity,  $\Delta P_t/\Delta L$  the total pressure gradient along the tube of radius  $a$ , and  $J$  is the molar flux (in moles per unit surface area and time). Integration of Eq. (2) over a distance  $L$  where the total pressure  $P_t$  drops from  $P_0$  to  $P$  gives

$$\frac{r}{\pi a^2} = J = \frac{a^2}{16RT\eta L} (P_0^2 - P^2). \quad (3)$$

When  $P_0$  is the pressure over the source and  $P = 0$ , Eq. (3) gives a distillation rate in vacuum. For  $P_0 = 10^{-4} \text{ atm}$ ,  $2a = 1.5 \text{ cm}$ ,  $T = 1000 \text{ K}$ ,  $\eta = 8 \times 10^{-4} \text{ g/(cm s)}$ , and  $L = 10 \text{ cm}$ , the distillation rate is  $r = 3.3 \times 10^{-3} \text{ mol per hour}$ .  $P_0$  may be less than the equilibrium pressure over the source due to kinetic limitations and the mass transport rate may be lower than might be expected from the equilibrium thermodynamic analysis alone.

For  $0.01 < Kn < 3$  a transitional, very complex mixed flow mode occurs, and theoretical calculations require an elaborate, direct simulation Monte Carlo (DSMC) method [7]. Therefore, for this  $Kn$  range we calculated the extreme mass flow rates determined by Eqs. (1) and (2).

When the oxide is being volatilized chemically (reaction with hydrogen, graphite, chalcogen, or hydrogen chalcogenide), the mass transport rate is limited by *diffusion* of the reactants through the vapor phase to and from the oxide condensed phase. The reaction products may diffuse out and deposit in a cooler part of the system and can be removed later under dynamic vacuum.

### 2.2. Thermochemical limitations

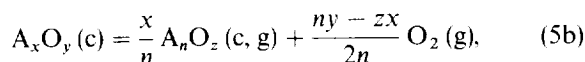
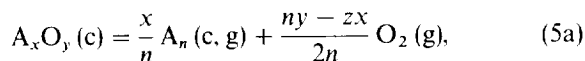
The rate of oxygen removal depends primarily on the volatility (partial pressures) of the original and related oxides and that of the matrix material. The simplest mechanism is

*molecular vaporization*

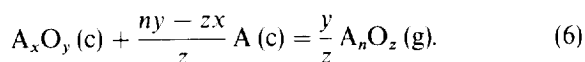


or

*dissociative vaporization*



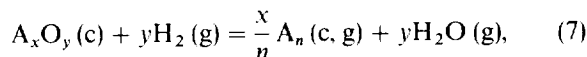
under vacuum, where 'c' denotes a condensed phase (solid 's' or liquid 'l'). In the presence of the element, condensed-phase vaporization may proceed through the reaction



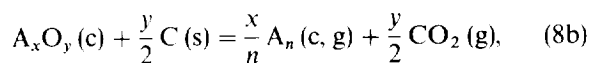
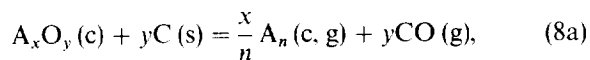
The oxide can be removed with only limited loss of the main compound when its partial pressure is about the same or higher than that of the matrix material. When the opposite occurs, an effective separation can be achieved by distillation of the matrix (leaving the less volatile oxide as a residue) but it requires (i) sufficiently high pressure of the distilled component (to make the purification process practical), and (ii) appropriately low pressure of the oxide. (For example, to reduce the amount of an oxide to the level of 1 ppm in the purified material, the pressure of the oxide should be about 6 orders of magnitude lower than that of the matrix.) However, oxides are usually present in the form of finely dispersed solid particles which can be easily carried/drifted along by the gas stream of the molecules or by an accidental electrostatic charge on the ampoule walls, recontaminating the distillation product. This can be minimized by separating the original source material from the purified product with special frits (and higher temperatures to compensate for related reduction in the flow rate). More volatile or less stable oxides of the element should be removed or decomposed first. The vaporization of oxides may be either significantly reduced (Eq. (5a): Bi<sub>2</sub>O<sub>3</sub>, ZnO, CdO, MnO, HgO) or increased (Eq. (6): Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, GeO<sub>2</sub>, SnO<sub>2</sub>) by the presence of a condensed phase of the respective element.

Removal of oxygen by chemical volatilization includes

*reduction by hydrogen*

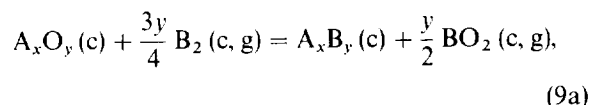


*reduction by graphite*



and

*formation of metal chalcogenides*



Vapor pressures of the elements were taken from Ref. [9], that of Sb<sub>4</sub>O<sub>6</sub> from Ref. [10]. We calculated the equilibrium partial pressures for reactions (1)–(5) from the dependence of the equilibrium constants *K* on the change of the Gibbs function,  $\Delta G$  ( $\Delta G = -RT \ln K$ ) using thermochemical data given in Refs. [11–13]. The equilibrium partial pressures for reactions (5a) and (5b) were computed both for stoichiometric and metal- or tellurium-saturated conditions. The equilibrium partial pressures over sulfur and selenium oxides (reaction (9a)) were calculated for the pressure of the elemental chalcogen of 1 atm or equal to its saturation pressure (for temperatures below the normal boiling point). For tellurides, the sign of the free energy for reaction (9a) (i.e. thermochemical stability of the tellurides) was computed.

### 3. Experimental procedures

The primary focus was on the minimum temperature under which a meaningful purification rate can be achieved. The rate of sublimation under dynamic vacuum (about 10<sup>-8</sup> atm or better) was determined experimentally using 0.5–1.0 mmol of the powder sample (particle size 1–30 μm) placed in silica glass ampoule (ID 15 mm). The processing

time was 0.5–72 h depending on the rate of vaporization. Not more than 50% of the initial charge was sublimed in each experiment. The material deposited at a distance of  $L = 10$  cm from the source. The amount of the deposit was weighted and its composition identified by physicochemical methods.

The reduction of oxides with hydrogen was investigated in silica glass ampoules (ID 20 mm) loaded at one end with the powdered oxide, evacuated, and back-filled with 1 atm hydrogen. The end with the oxide sample was placed in a furnace. The water formed by reaction (7) condensed at a distance of 15–20 cm from the source. In the first series of experiments (with source amount 7 mmol) the temperature of the sample was gradually increased at a rate of about 400°C per hour and the change of the total pressure with temperature was recorded. The initial increase in the pressure due to thermal expansion was followed by a pressure drop (at  $T > T_0$  where  $T_0$  represents the onset of reduction) due to condensation of water. In the second series of experiments the oxide (0.8–1.0 mmol) was annealed at selected temperature. The rate of reduction was determined from the rate of the pressure decrease with time.

Reduction by graphite was investigated in sealed silica ampoules (ID 15 mm, length 10 cm) loaded with 0.8–1 mmol of a given oxide and a necessary amount of graphite. The graphite was in the form of a solid piece, a fine powder, or a thin film deposited on part of the ampoule inner wall prior to loading. The ampoule was sealed under vacuum and annealed. The annealed ampoule was opened under water, the volume of the resulting gas bubble (carbon oxides) measured and the degree of reduction calculated assuming thermochemical equilibrium between CO and CO<sub>2</sub> at the annealing temperature.

Reactions with chalcogens (reaction (9a)) were tested for several oxides: 1 mmol of a given oxide (fine powder) and a stoichiometric amount of the chalcogen were sealed under vacuum in a fused silica ampoule and annealed at a given temperature for 1 h (longer in several cases, cf. Section 4.1.4, Table 5). The temperature was increased in 100°C increments until signs of reaction were noticed. The percentage of the reduced oxide was determined from the amount of unreacted chalcogen in the ampoule.

## 4. Results and discussion

### 4.1. Purification rates

#### 4.1.1. Sublimation under dynamic vacuum

Equilibrium partial pressures over the elements and oxides are shown in Fig. 1a–Fig. 1j (the partial pressures of SnO, GeO, and PbO include contributions from the multimers (MeO)<sub>n</sub>). Measured and predicted rates of vaporization of the elements and their oxides under dynamic vacuum are summarized in Table 1a and Table 1b. In most cases the vaporization rates are within a factor of 4 or within the range of our theoretical predictions (cf. Section 2). In some cases kinetic limitations exist, primarily at higher equilibrium pressures (predicted rates > 10 mmol/h) and/or lower process temperatures (< 500°C). Relatively low purification rates in two-condensed-phase processes (cf. Eq. (6)) were found to be caused by a limited contact between the phases. Test experiments showed, that an increase in the amount of the source by a factor of ten increases the vaporization rate by less than a factor of two.

#### 4.1.2. Reduction by hydrogen

Equilibrium partial pressures of water (Eq. (7)) as a function of temperature calculated for an initial hydrogen pressure  $P^0(\text{H}_2) = 1$  atm are given in Fig. 2. In most cases equilibrium partial pressures of the related elements are low, thus a condensed phase of the element forms and the reduction process does not depend on the initial presence of excess element in the source material. The opposite situation occurs only for ZnO and CdO (Fig. 2). Our experimental results are summarized in Table 2. The rate of reduction at  $T_0$  is very low, and increases at higher temperatures. The reduction process depends strongly on the grain size of the oxide: reduction rates of the solid chunk and powdered TeO<sub>2</sub> differ by more than one order of magnitude (Table 2). The rate decreases as the process progresses and complete reduction requires considerably more time than the initial reduction rates would indicate (Table 2). As expected from our thermochemical calculations (Fig. 2), manganese oxide cannot be reduced by hydrogen under our experimental conditions. The equilibrium partial

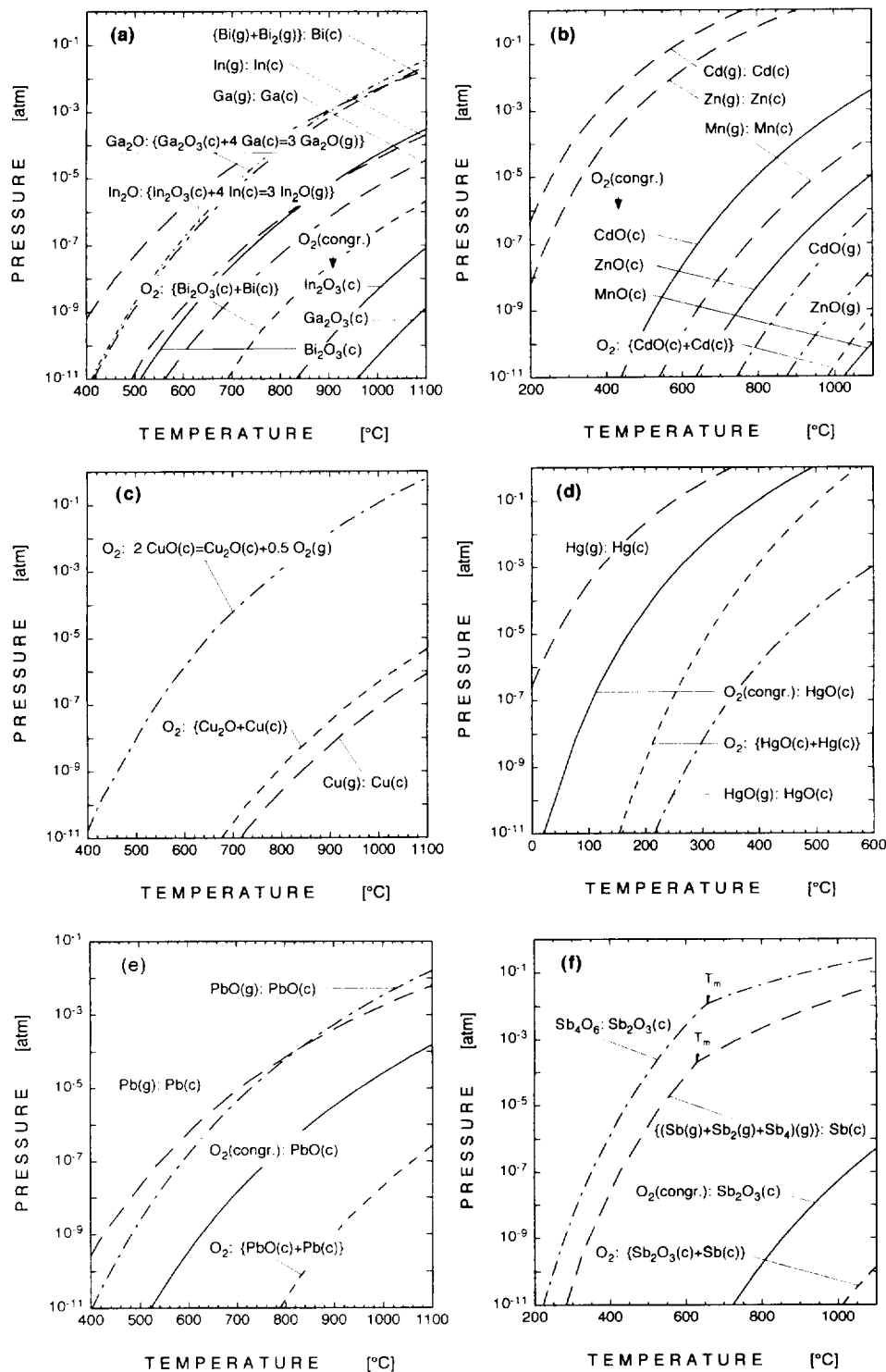


Fig. 1. Equilibrium partial pressures over elements and their oxides. The pressures of oxygen under metal-saturated conditions not shown in the graphs are less than  $10^{-11}$  atm.

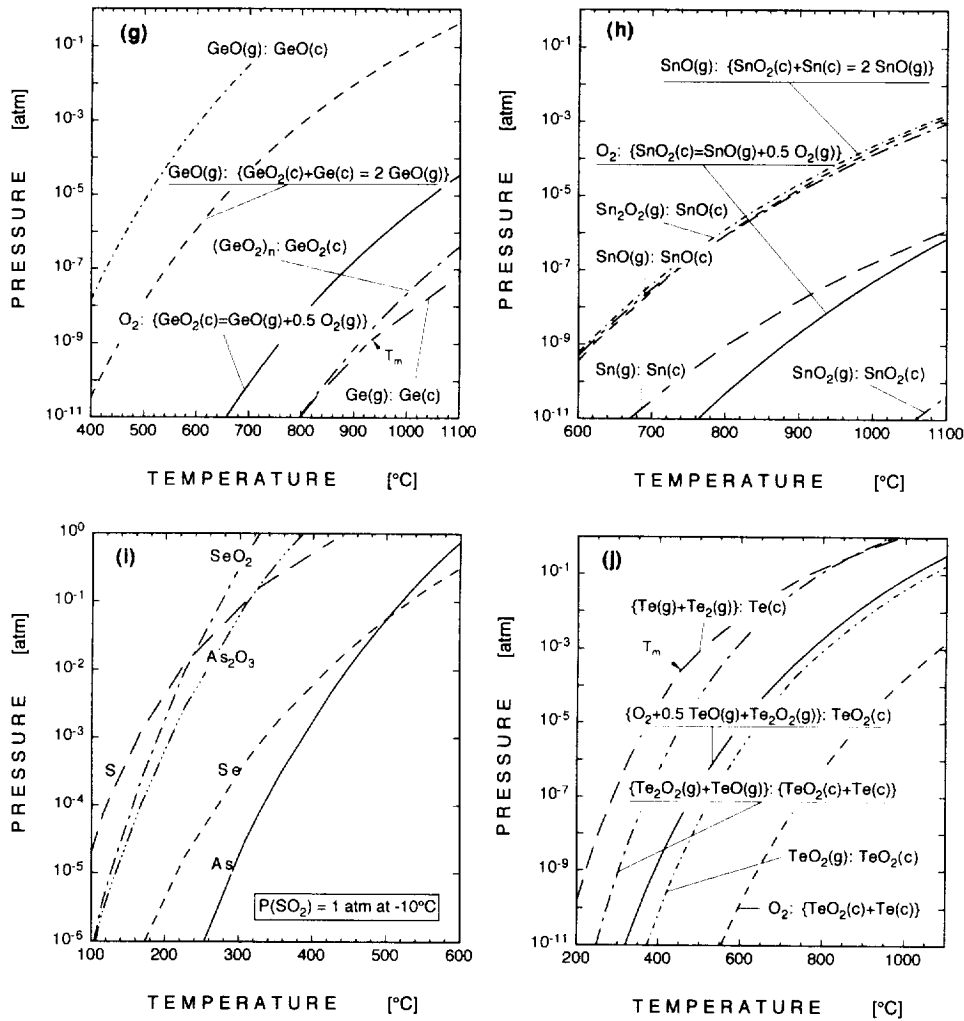


Fig. 1. (Continued).

pressure of water over  $\text{Ga}_2\text{O}_3$  and  $\text{ZnO}$  (under congruent vaporization, Fig. 2) is very low. Under these conditions, a chemical vapor transport (CVT) process sets in: the products of the reaction of hydrogen with the oxides are transported to a cooler part of the system where a reversal of the process takes place and the oxide deposits. Reduction of other oxides leads to relatively high  $\text{H}_2\text{O}$  pressures. Thus, the water is easily removed from the source region and condenses in a cooler part of the system, and a CVT process is practically not

observed. The released elements (Eq. (7)) have relatively low vapor pressure under the reduction conditions and (except for Te) remain in the source region. They have to be removed (if necessary) in a separate process.

Reduction by hydrogen requires only a small quantity of gas (a few  $\text{cm}^3$  of hydrogen under normal conditions for  $10^{-4}$  mol of an oxide), depends on the pressures of  $\text{A}_n$  (or the presence of A (c)) and hydrogen, and can be usually performed in a closed system.



Table 1

Vaporization of (a) metal and (b) non-metal oxides under dynamic vacuum; ID = 15 mm,  $\Delta L = 10$  cm,  $n = 0.5$ –1 mmol

Oxide	T (°C)	n/t (mmol/h)	
		Theoretical	Experimental
<i>(a) Metal oxides</i>			
Bi	750/600	2.2/( $1.5 \times 10^{-3}$ –0.14)	3.9/0.018
Bi <sub>2</sub> O <sub>3</sub>	800 <sup>a</sup> /700 <sup>a</sup> /600 <sup>a</sup>	0.058/( $2.9 \times 10^{-3}$ )/ $8.3 \times 10^{-5}$	0.11 <sup>b</sup> /0.003 <sup>b</sup> / < 0.001 <sup>b</sup>
Cd	300	5–11	0.61 <sup>c</sup>
CdO	900/800	(10–23)/(0.12–2.3)	2.0 <sup>c</sup> /0.23
Cu	1000	0.012	0.050
Cu <sub>2</sub> O	1000 <sup>a</sup>	0.096	0.035
Ga	1000	(0.015–0.80)	0.14
Ga <sub>2</sub> O <sub>3</sub>	1000	$7.6 \times 10^{-6}$	< 0.0002
Ga <sub>2</sub> O <sub>3</sub> /Ga	900/800	434/4.3	0.89 <sup>d</sup> /0.30 <sup>d</sup>
Ge	1000	$7.6 \times 10^{-4}$	0.002
GeO	700	> $10 \times 10^4$	> 4
GeO <sub>2</sub>	1000	(0.01–0.7)	< 0.00003 <sup>c</sup>
GeO <sub>2</sub> /Ge	930	$2 \times 10^5$	> 5 <sup>d</sup>
Hg	195/175/125/110	$4 \times 10^5/1 \times 10^5/3 \times 10^3/750$	15 <sup>c</sup> /3.2 <sup>c</sup> /1.8 <sup>c</sup> /0.4 <sup>c</sup>
HgO	515/460/210	> 70	2.6 <sup>c</sup> /0.42 <sup>c</sup> /0.013 <sup>c</sup>
In	1000/800/770	(0.67–4.1)/0.076/0.037	1.6/0.18/0.04
In <sub>2</sub> O <sub>3</sub>	1000	$6.1 \times 10^{-4}$	$4.2 \times 10^{-4}$
In <sub>2</sub> O <sub>3</sub> /In	900/800	147/(1.7–5.4)	6.5 <sup>d</sup> /0.65 <sup>d</sup>
Mn	1000 <sup>a</sup>	0.25–3.8	0.64
MnO	1000	$1.8 \times 10^{-6}$	< 0.0001
Pb	800/700/600	(2.5–6.3)/(0.06–0.9)/0.063	3.6/0.30/0.0004 <sup>c</sup>
PbO	800 <sup>a</sup> /700 <sup>a</sup> /600 <sup>a</sup> /500	(2.3–39)/(0.01–2.7)/0.015/ $2.6 \times 10^{-4}$	1.54/0.38/ $6.2 \times 10^{-3}$ / $5.8 \times 10^{-5}$
Sb	500/450	( $9 \times 10^{-3}$ –0.38)/0.043	0.14/0.024
Sb <sub>2</sub> O <sub>3</sub>	390	( $3 \times 10^{-3}$ –0.055)	0.059
Sn	1000	0.015	0.0068
SnO	800/700	0.27/0.01	0.24/0.041
SnO <sub>2</sub>	1000	0.010	0.010
SnO <sub>2</sub> /Sn	1000/760	19.4/0.032	(> 0.7) <sup>d</sup> /0.020
Zn	430/400	72/12	1.0 <sup>c</sup> /0.44 <sup>c</sup>
ZnO	1000	( $1.6 \times 10^{-3}$ –0.31)	0.0071
<i>(b) Non-metal oxides</i>			
As	345/310	120/(3.1–4.4)	2.9 <sup>c</sup> /1.1
S	130	250	~ 25 <sup>c</sup>
Se	240	(3.6–4.1)	~ 5
Te	420/340	22/(0.013–0.21)	1.7 <sup>c</sup> /0.45
TeO <sub>2</sub>	700/600	24/(0.16–0.76)	3.0 <sup>c</sup> /0.14
TeO <sub>2</sub> /Te	460/420	(0.13–1.5)/0.003–0.18)	< 0.003 <sup>c</sup>

<sup>a</sup>The source reacted with fused silica.<sup>b</sup>Some of the vaporized material reacted with fused silica.<sup>c</sup>Apparent kinetic limitations to vaporization.<sup>d</sup>Vaporization rate reduced by limited contact between the reacting condensed phases.<sup>e</sup>Sublimation performed in alumina tubing.

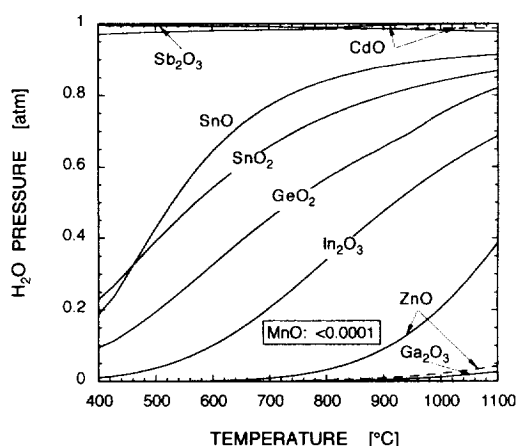


Fig. 2. Vapor pressure of water in equilibrium with oxides. Initial pressure of hydrogen is  $P^0(\text{H}_2) = 1$  atm. Solid lines (—), in the presence of saturated pressure of respective element; dashed lines (---), under congruent conditions. Equilibrium partial pressures of water in the presence of  $\text{PbO}$ ,  $\text{HgO}$ ,  $\text{TeO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Cu}_2\text{O}$ , and  $\text{CuO}$  are more than 0.999 atm.

#### 4.1.3. Reduction by graphite

The calculated equilibrium total pressure of  $\text{CO}$  and  $\text{CO}_2$  as a function of temperature (reactions (8a) and (8b)) is plotted in Fig. 3 for various oxides. From these curves one would expect that only  $\text{MnO}$ ,  $\text{ZnO}$  and  $\text{Ga}_2\text{O}_3$  are not significantly reduced below about  $700^\circ\text{C}$ . The experimental results in Table 3 show otherwise. Significant reductions in oxide content required much higher temperatures than anticipated, and  $\text{ZnO}$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{MnO}$  showed no noticeable reduction even after annealing at  $1000^\circ\text{C}$  for 20–35 h (Table 3). Apparently, the reactions are kinetically limited at lower temperatures. Furthermore, with intimate mixtures of graphite and oxide powders, the reaction rates were highest. When chunks of graphite were used, the rates dropped. With graphite films, which were physically separated from the oxides, the rates dropped even further. From this it is apparent that the reduction rates were controlled by the mass transport of carbon dioxide from the oxide to the graphite and the corresponding flow of carbon monoxide in the opposite direction (Eq. (8a) and Eq. (8b)). Note that the temperatures required for purification with graphite were typically higher

Table 2

The rate of reduction by hydrogen; initial pressure,  $P^0(\text{H}_2) = 1$  atm, amount of the source,  $n = 0.8$ – $1$  mmol;  $T_{0.5}$  and  $t_{0.98}$  are the times after which 50% and > 98%, respectively, of the initial source is reduced.  $T_o$  is the temperature of the onset of reduction,  $(n/t)_{\text{init}}$  is the average reduction rate in the first 10 min of the process

Oxide	$T_o$ ( $^\circ\text{C}$ )	$T$ ( $^\circ\text{C}$ )	$(n/t)_{\text{init}}$ (mmol/h)	$t_{0.5}$ (min)	$t_{0.98}$ (min)
$\text{Bi}_2\text{O}_3$	380	380	0.3	< 10	75
		460			
$\text{CdO}$	290	290	< 0.3	30	150
		340			
$\text{Cu}_2\text{O}$	290	300	1.0	< 10	75
		325			
$\text{CuO}$	180	180	1.7	< 10	75
		220			
$\text{Ga}_2\text{O}_3$	a	900	0.06	< 10	75
		1000			
$\text{GeO}_2$	590	600	0.75	30	150
		635			
$\text{HgO}$	290	300	$\leq 0.5$	< 5	< 30
		350			
$\text{In}_2\text{O}_3$	540	540	0.15	40	150
		570			
$\text{MnO}$	> 1000	--	--	--	--
$\text{PbO}$	420	420	< 0.3	< 5	30
		450			
		500			
		570			
$\text{Sb}_2\text{O}_3$	570	570	0.3	< 10	90
		640			
$\text{SnO}$	490	490	< 0.3	10	60
		600			
$\text{SnO}_2$	460	460	< 0.2	< 10	90
		650			
$\text{TeO}_2$	560 <sup>b</sup>	600	0.3 <sup>b</sup>	< 10	90
		650			
		460			
		560			
$\text{ZnO}$	a	700	0.4	< 5	60
		770			
		770			
		2.0			

<sup>a</sup>No decrease in  $\text{H}_2$  pressure. CVT process (see text).

<sup>b</sup>Solid chunk source.

than those needed for reduction by hydrogen and reaction with chalcogens (see below).

Obviously, removal of oxides by graphite is not an effective purification method. In addition, graphite may be an undesired component which cannot be easily removed from the system. Also, reaction of even trace amounts of graphite and

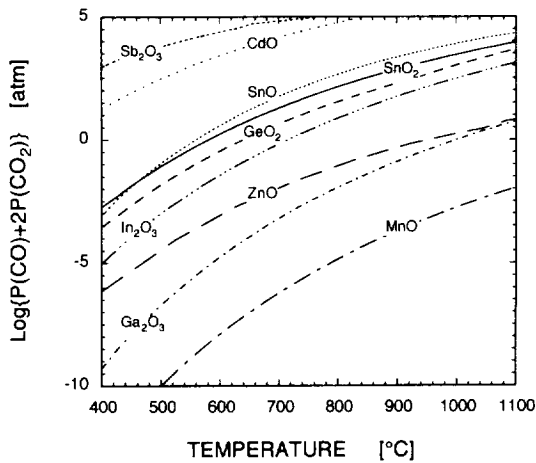


Fig. 3. Equilibrium partial pressures of 'oxygen' ( $P(\text{CO}) + 2P(\text{CO}_2)$ ) in equilibrium with graphite. The total pressure of carbon oxides in the presence of  $\text{Bi}_2\text{O}_3$ ,  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{HgO}$ ,  $\text{PbO}$ , and  $\text{TeO}_2$  is  $\log\{P(\text{CO}) + 2P(\text{CO}_2)\} > 5$ .

oxide impurity(ies) may affect the amount of residual gas in closed systems and may have a profound effect particularly on PVT processes. In such cases the oxides should be removed before the material is sealed in the growth ampoule. However, it has also been observed that a presence of a piece of graphite in the ampoule during directional solidification of germanium reduces sticking of the material to the silica glass wall [14]. Apparently, the graphite helped in reducing the oxides present in the original source material.

4.1.4. Removal by chalcogens and hydrogen chalcogenides

The results of our thermochemical calculations for temperatures up to 1100°C (within the range of existence of respective phases) are shown in Table 4. All oxides can be expected to be effectively reduced by sulfur. Selenium and tellurium may reduce only a limited number of oxides (Table 4). Our experimental results are given in Table 5. (The reduction rates are similar when three times larger amounts of the source material are used.) As theoretically predicted, the reactions with the chalcogens proceed already at moderate temperatures (400–500°C, Table 5). Sulfur and selenium react

Table 3  
Oxide reduction rates with graphite

Oxide	Graphite	T (°C)	Time (h)	Reduction (%)	
$\text{Bi}_2\text{O}_3$	p	600	1	< 1	
		700	1	40	
		800	1	50	
		900	1	> 80	
CdO	c	900	1	15	
		p	900	19	< 2
		1000	1	> 70	
Cu <sub>2</sub> O	p	1000	1	30	
		1000	21	60	
		f	1000	1	< 2
		1000	1	< 5	
$\text{Ga}_2\text{O}_3$	p	1000	35	< 2	
		1000	1	< 2	
$\text{GeO}_2$	p	900	19	< 1	
		1000	1	3	
HgO	c	1000	21	25	
		p	500	1	15
$\text{In}_2\text{O}_3$	p	600	1	> 80	
		900	20	< 5	
		1000	1	10	
		1000	17	30	
MnO	p	1000	20	< 1	
		1000	20	< 1	
PbO	p	600	1	< 1	
		700	1	30	
		f	700	1	< 2
$\text{Sb}_2\text{O}_3$	p	900	1	< 2	
		900	20	25	
		1000	1	15	
SnO	p	800	1	< 2	
		f	1000	1	8
$\text{TeO}_2$	p	600	1	10	
		700	1	> 80	
ZnO	p	1000	35	< 2	

(p) – powder; (c) – chunk; (f) – film.

more effectively than tellurium, apparently due to their higher volatility relative to that of Te. For 500°C and above, the dependence of the reaction rate on temperature is relatively small (Table 5). The annealing time may have only limited effect on the process (Table 5). The weak dependence of the reaction rate on temperature and time suggests that the rate of reduction of the oxides by chalcogens may be limited by diffusion in the solid oxide/chalcogenide particles.

Table 4

Reduction of oxides by chalcogens;  $P(\text{SO}_2)$  and  $P(\text{SeO}_2)$  are equilibrium partial pressures (Eq. (9a)) in the presence of the chalcogen condensed phase (below the normal boiling point temperature,  $T_b$ ) or under 1 atm of chalcogen (above  $T_b$ );  $\Delta G$  is the Gibbs energy for reaction of a given oxide with tellurium

Oxide	$P(\text{SO}_2 + \text{SO})^a$	$P(\text{SeO}_2 + \text{SeO})^a$	$\Delta G^b$
$\text{Bi}_2\text{O}_3$	+	c	$> 0$
$\text{CdO}$	+	$> 1$ for $T > 420^\circ\text{C}$	$< 0$ for $T < 580^\circ\text{C}$
$\text{Cu}_2\text{O}$	+	+	$< 0$
$\text{Ga}_2\text{O}_3$	$> 1$ for $T > 205^\circ\text{C}$	–	$> 0$
$\text{GeO}_2$	$> 1$ for $T > 420^\circ\text{C}$	–	
$\text{HgO}$	+	+	$< 0$
$\text{In}_2\text{O}_3$	$> 1$ for $T > 180^\circ\text{C}$	–	$> 0$
$\text{MnO}$	+	–	$> 0$
$\text{PbO}$	+	$> 1$ for $T > 400^\circ\text{C}$	$< 0$ for $T < 880^\circ\text{C}$
$\text{Sb}_2\text{O}_3$	+	–	$> 0$
$\text{SnO}$	+	–	$> 0$
$\text{ZnO}$	+	–	$> 0$

<sup>a</sup>(+)  $P > 10$  atm; (–)  $P < 0.01$  atm.

<sup>b</sup> $\text{Me}_x\text{O}_y(\text{c}) + 1.5 Y \text{Te}(\text{c}) = \text{Me}_x\text{Te}_y(\text{c}) + Y/2\text{TeO}_2(\text{c})$ .

<sup>c</sup> $P(\text{max}) \approx 0.09$  atm at  $T = 685^\circ\text{C}$ .

Hydrogen chalcogenides (or an appropriate mixture of chalcogen and hydrogen) are more effective reducers than the elemental chalcogens. Our calculations show that the ratio of the equilibrium partial pressure of  $\text{H}_2\text{O}$  and  $\text{H}_2$  for reaction (9b) is well above unity for all oxides and chalcogenides except for  $\text{MnTe}$ , where it is between 0.5 and 0.8 (for  $T = 300$ – $1100^\circ\text{C}$ ). Selected test experiments confirmed these predictions: even reduction of  $\text{MnO}$  by hydrogen in the presence of tellurium was observed at temperature as low as  $600^\circ\text{C}$ , while a reaction of  $\text{MnO}$  with tellurium without hydrogen was not observed even after 20 h annealing at  $1000^\circ\text{C}$  (Table 5).

The formation of chalcogenides depends on the pressure of the chalcogen ( $\text{B}_2$ ) or hydrogen chalcogenide ( $\text{H}_2\text{B}$ ) (Eq. (9a) and Eq. (9b), respectively) and can usually be performed in closed ampoules. The process is technically less convenient than purification with  $\text{H}_2$  but may be useful in some systems.

#### 4.2. Specific metal oxides

##### 4.2.1. Bismuth, gallium, and indium

The three elements form stable oxides of the formula  $\text{Me}_2\text{O}_3$ , which vaporize dissociatively.

Table 5

The rate of reduction of metal oxides by corresponding chalcogens

MeX	$T_{\text{ann}} (^\circ\text{C})$	$\text{Time}_{\text{ann}} (\text{h})$	Percentage of oxide reduced %
$\text{CdSe}$	500	1	$> 95$
	500	1	50
$\text{CdTe}$	500	4	40
	700	1	65
$\text{HgTe}$	500	1	50
$\text{MnS}$	600	1	45
	800	2	80
$\text{MnTe}$	1000	15	$< 1$
$\text{PbTe}$	500	1	50
	500	4	60
	700	1	85
$\text{ZnS}$	400	1	30
	500	1	80
	500	4	$> 95$

$\text{BiO}(\text{c})$  and  $\text{Bi}_2\text{O}_5(\text{c})$  decompose to  $\text{Bi}_2\text{O}_3$  below  $400^\circ\text{C}$ ,  $\text{In}_2\text{O}(\text{c})$  and  $\text{Ga}_2\text{O}(\text{c})$  vaporize under vacuum at temperatures well below  $500^\circ\text{C}$ . Congruent decomposition pressures are low (Fig. 1a), thus the removal of  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  oxides under dynamic vacuum requires high temperatures and is

slow.  $\text{Bi}_2\text{O}_3$  requires temperatures at which even the vapors of the oxide react with the fused silica (Table 1a). Rapid removal of  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  occurs in the presence of gallium and indium, respectively (Fig. 1a and Table 1a).

The purification of bismuth by vacuum distillation requires a prior reduction of  $\text{Bi}_2\text{O}_3$ . Removal of  $\text{Ga}_2\text{O}_3$  by hydrogen is relatively slow (CVT process, cf. Section 4.1.2) and requires high temperatures (Table 2). The reduction of  $\text{Bi}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  by  $\text{H}_2$  proceeds at moderate temperatures (Table 2). The oxides can also react with sulfur and hydrogen chalcogenides (Table 4). A noticeable reduction of  $\text{Bi}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  by graphite requires higher temperatures ( $> 700^\circ\text{C}$  and  $> 1000^\circ\text{C}$ , respectively).  $\text{Ga}_2\text{O}_3$  does not show any measurable reduction even after 35 h annealing at  $1000^\circ\text{C}$  (Table 3).

#### 4.2.2. Cadmium, manganese, and zinc

Stable oxides of the elements have the formula  $\text{MeO}$  and vaporize mainly dissociatively (Fig. 1b).  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{Mn}_2\text{O}_7$  decompose to  $\text{MnO}$  under high vacuum at temperatures well below  $1000^\circ\text{C}$ .  $\text{CdO}$  and  $\text{ZnO}$  can be removed by congruent vaporization at high temperatures (Fig. 1b and Table 1a). The pressure of oxygen under metal-saturated conditions is very low and purification of the metals by vacuum distillation is possible. Reaction of manganese with fused silica at high temperatures may require an alternate vessel material, e.g., alumina. Hydrogen reacts differently with each of the oxides.  $\text{CdO}$  gets reduced already around  $300^\circ\text{C}$ .  $\text{ZnO}$  is removed by means of a CVT process at elevated temperature.  $\text{MnO}$  is not reduced at all. The oxides can be removed by sulfur and hydrogen chalcogenides.  $\text{CdO}$  can also be removed by selenium and tellurium (Tables 4 and 5).  $\text{CdO}$  is reduced by graphite at  $1000^\circ\text{C}$ , but no apparent reduction of  $\text{ZnO}$  and  $\text{MnO}$  is observed at that temperature even after a long annealing (Table 3).

#### 4.2.3. Copper

There are two copper oxides,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ .  $\text{CuO}$  decomposes easily to  $\text{Cu}_2\text{O}$  which, in turn, decomposes into copper and oxygen (Fig. 1c). The decomposition partial pressures over  $\text{Cu}_2\text{O}$  are

low, and the rate of removal of oxygen requires high temperatures and is slow (Table 1a). The saturation pressure of  $\text{Cu}$  is lower than that for stoichiometric dissociative vaporization of  $\text{Cu}_2\text{O}$  and  $\text{Cu(c)}$  phase forms in the source region. Condensing copper gets 'fused' into silica in the deposition zone apparently by a process of diffusion into the solid. The equilibrium pressure over  $\text{Cu(c)}$  is too low for an effective purification by vacuum distillation under practical laboratory conditions. Removal of the oxides by hydrogen, chalcogens, hydrogen chalcogenides, and graphite is feasible and can be accomplished at relatively low temperatures (Tables 2–4 and Figs. 2 and 3).

#### 4.2.4. Mercury

Of the two oxides,  $\text{Hg}_2\text{O}$  decomposes at  $100^\circ\text{C}$ .  $\text{HgO}$  vaporizes primarily dissociatively (Fig. 1d) and can be removed below  $400^\circ\text{C}$ . The vaporization rate of  $\text{Hg}$  (Table 1a) is much lower than expected from equilibrium partial pressures shown in Fig. 1d. The partial pressure of oxygen is not sufficiently low for an effective direct purification of mercury by vacuum distillation, thus a prior reduction of the oxide (by hydrogen) may be necessary. Removal of oxygen by hydrogen, chalcogens, hydrogen chalcogenides, and graphite is feasible (Tables 2–4 and Figs. 2 and 3).

#### 4.2.5. Lead

The most stable lead oxide is  $\text{PbO}$  ( $\text{Pb}_2\text{O}$ ,  $\text{Pb}_2\text{O}_3$ ,  $\text{PbO}_2$ , and  $\text{Pb}_3\text{O}_4$  decompose to  $\text{PbO}$  below  $400^\circ\text{C}$  under vacuum). This oxide vaporizes primarily molecularly (Fig. 1e). Removal of oxygen should occur mainly through  $\text{PbO}$  species and at moderate temperatures (Fig. 1e). However, our experiments showed that the vaporization occurs largely through dissociation of  $\text{PbO}$  (deposition of  $\text{Pb(c)}$ ) and at vaporization rates consistent with the congruent dissociation pressure of  $\text{PbO}$ . Lead oxide reacts easily with fused silica at temperatures as low as  $600^\circ\text{C}$  (Table 1a). Thus, an alternate to fused silica material may be required for the purification vessel. Vacuum distillation of  $\text{Pb}$  may require a prior reduction of  $\text{PbO}$  with hydrogen. Removal of oxygen by hydrogen, chalcogens, hydrogen chalcogenides, and graphite is feasible (Tables 2–4 and Figs. 2 and 3).

#### 4.2.6. Antimony

The stable oxide is  $\text{Sb}_2\text{O}_3$  ( $\text{SbO}_2$  and  $\text{Sb}_2\text{O}_5$  decompose to  $\text{Sb}_2\text{O}_3$  below  $800^\circ\text{C}$ ). This oxide vaporizes molecularly in the form of  $\text{Sb}_4\text{O}_6$  species [10] and can be easily removed under vacuum at temperatures as low as  $400^\circ\text{C}$  (Fig. 1f and Table 1a). Removal of oxygen by hydrogen, sulfur, hydrogen chalcogenides, and graphite is possible (Tables 2–4 and Figs. 2 and 3).

#### 4.2.7. Germanium

Germanium monoxide,  $\text{GeO}$ , is relatively volatile and vaporizes molecularly (Fig. 1g). However, the congruent sublimation of  $\text{GeO}_2$  requires high temperatures and is very slow (Table 1a), apparently due to some kinetic limitations. Much faster vaporization can be obtained in the presence of Ge condensed phase (Fig. 1g and Table 1a). The partial pressure of germanium is very low, and vacuum distillation is not feasible. Removal of  $\text{GeO}_2$  (and  $\text{GeO}$ ) by hydrogen, sulfur, hydrogen chalcogenides, and graphite is possible (Tables 2–4 and Figs. 2 and 3).

#### 4.2.8. Tin

Similar to germanium, tin forms two oxides: more volatile  $\text{SnO}$  and much less volatile  $\text{SnO}_2$  (Fig. 1h). Removal of  $\text{SnO}$  is fast, that of  $\text{SnO}_2$  is much slower (Fig. 1h and Table 1a). Removal of  $\text{SnO}_2(\text{c})$  is facilitated by the presence of Sn condensed phase (Fig. 1h and Table 1a). Saturation pressure of tin is low and vacuum distillation is very slow. The oxides can be removed by hydrogen, sulfur, hydrogen sulphide, and graphite (Tables 2–4 and Figs. 2 and 3).

#### 4.3. Specific non-metal oxides

Equilibrium partial pressures over chalcogens and arsenic and their most stable oxides are shown in Fig. 1i and Fig. 1j. Except for  $\text{TeO}_2$ , the oxides vaporize molecularly and are more volatile (normal boiling point below  $400^\circ\text{C}$ ) than the respective elements (Fig. 1i). The oxides can usually be removed simultaneously with removal of metal oxides from compound materials. Purification of S, Se, and As can easily be achieved by vacuum annealing or distillation (Table 1b).

Partial pressures over congruent  $\text{TeO}_2(\text{c})$  ( $\text{TeO}$ ,  $\text{Te}_2\text{O}_2$ ,  $\text{O}_2$ , and  $\text{TeO}_2$  species) are lower than that of elemental tellurium (Fig. 1j) ( $\text{TeO}(\text{c})$  and  $\text{TeO}_3(\text{c})$  decompose below  $400^\circ\text{C}$ ). Therefore, an effective removal of oxygen may require reduction of  $\text{TeO}_2$  by hydrogen. The presence of  $\text{Te}(\text{c})$  should increase the equilibrium pressures over  $\text{TeO}_2(\text{c})$  (Fig. 1j). However, our tests did not show any noticeable effect of  $\text{Te}(\text{c})$  on removal of  $\text{TeO}_2$  (Table 1b), apparently due to some kinetic limitations under our experimental conditions.

### 5. Summary

The removal of oxides from materials can be accomplished using different physical and/or chemical processes and procedures. This paper illustrates the potentials and limitations of several basic techniques that can be used for that purpose in research laboratories and industrial technological processes. Real experimental conditions may differ from those used in this work and each specific system should be critically assessed. For example, oxide impurities in source elements and compounds are usually present in a finely dispersed form and their removal may proceed more rapidly than under our experimental conditions. On the other hand, vaporization rates may be lower when only a very small amount of the oxide is present (left) in the system. The rate of the purification process may also be reduced if the oxide is trapped inside a solid matrix material grain. Therefore, powdered solid materials should be used. Also, this work addresses only the direct removal of oxides (oxygen) from the related element (e.g. removal of  $\text{Bi}_2\text{O}_3/\text{O}_2$  from liquid/solid bismuth). Removal of a given oxide from an unrelated element or compound (e.g.  $\text{ZnO}$  in liquid/solid cadmium or cadmium telluride) requires additional considerations. These concern, primarily, the volatility and chemical reactivity of the material with respect to the oxide; for example, a less stable oxide may form a more stable one in reaction with the matrix compound.

Purification by vacuum annealing is a subject to specific thermochemical (low pressure(s)), kinetic, and geometrical limitations to mass flow. Therefore, removal of oxides by active gaseous species

(hydrogen, chalcogen, hydrogen chalcogenide) can be recommended.

The main objective of our work was to determine borderline conditions required for a given process. In many cases other process parameters (e.g. higher temperature) can be used and the purification process can proceed faster than reported in this work.

### Acknowledgements

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*Original material.* Submission of a manuscript implies it is not being simultaneously considered for publication elsewhere and that the authors have obtained the necessary authority for publication.

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Original research papers, Letters to the Editors and Priority communications are welcome. They should contain an Abstract (of up to 200 words) and a Conclusion section, which particularly in the case of theoretical papers translates the results into terms readily accessible to most readers.

As a guideline: *experimental papers* should not be longer than 16 double-spaced typed pages, and 8 figures + tables; for *theoretical papers* a maximum of 20 pages and 10 figures + tables is suggested.

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### Manuscript preparation

Contributions may be written in English, French or German. They should have an abstract in English. The paper copies of the text should be prepared with double line spacing and wide margins, on numbered sheets.

*Structure.* Please adhere to the following order of presentation: Article title, Author(s), Affiliation(s), Abstract, PACS codes and keywords, Main text, Acknowledgements, Appendices, References, Figure captions, Tables.

*Corresponding author.* The name, complete postal address, telephone and fax numbers and the e-mail address of the corresponding author should be given on the first page of the manuscript.

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Elsevier Science B.V., J. Crystal Growth  
Issue Management Physics  
and Materials Science  
P.O. Box 2759, 1000 CT Amsterdam  
The Netherlands  
Fax: +31 20 485 2319/ +31 20 485 2704  
E-mail: matsci-de-f@elsevier.nl

