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The Influence of Atmosphere on Oxides Crystal Growth

Morteza Asadian
Iranian National Center of Laser Science and Technology,
Tehran,
Iran

1. Introduction

Oxide single crystals are known for wide application in electronics and optical industries, e.g. lasers, substrates, scintillators, nonlinear and passive optical devices (Brandle, 2004). The Czochralski technique has become an important method of choice for the growth and production of many bulk oxide materials owing to the possibility of growing crystals with large size, core free with good optical quality, and a high concentration of dopant, e.g., Nd^{3+}, Yb^{+3} with better homogeneity (Zhaobing et al., 2007; Albrecht et al., 1998).

Numerous researchers (Dupret and Bogaert, 1994; Cockayne et al., 1976; Valentino and Brandle, 1974; Brandle, and Barns, 1974; Jacobs et al., 2007; Mateika et al., 1982; Piekarczyk and Pajaczkowska, 1979) have studied the effect of different parameters on the quality of oxide crystals grown by Czochralski technique. They found that Crystal growth atmosphere composition and melt stoichiometry are strongly influenced on the quality of crystals as well as solid-liquid interface shape.

However, the growth of oxides such as $Gd_3Ga_5O_{12}$ [Brandle et al., 1972], ZnO [Klimm et al., 2008a], SrLaGaO4 [Pajaczkowska et al., 2001], single crystals by standard melt growth techniques are difficult due to their high melting point and thermal decomposition upon heating. Otherwise, if the composition of melt would be serious, the chemical composition of these oxides melt will depart from the congruent point and superfluous components would become the harmful impurities for crystal growth.

Due to the volatilization of oxide melts and the necessity of an oxidizing atmosphere, the crucible that contains the melt should consist of a noble metal. The only materials that have been found to tolerate these violent conditions are the platinum group of metals and their alloys (Day, 1963; Cockayne, 1974). Although the growth from platinum crucible can be performed in presence of oxygen, unfortunately, platinum with T_m=2042 K and its alloys cannot use for mostly oxides because of their high melting point (Darling et al., 1970). Very often platinum or alloys of platinum are used only for oxides with low melting point (T<1850 K) (Uitert, 1970). Actually, it is necessary to choose materials of higher melting point, such as the rhodium-platinum alloys, or rhodium or iridium metals (Cockayne, 1968). Owing to a high melting point and high mechanical strength even at T> 2250 K° (Handley,1986), iridium crucible are widely used for growing high melting oxides such as GGG, Al_2O_3 and ZnO. It is important to note that, iridium is more sensitive to

oxidation than platinum or rhodium (Weiland et al., 2006), especially in the medium temperature (~870-1000 K°) as the metal would oxidize to IrO_2 (s) (Asadian et al., 2010). Consequently, the addition of oxygen to the furnace chamber reacts with iridium crucible at medium temperatures and it complicates the process of crystallization (Lipinska et al., 2009).

The ceramic oxide crucibles are usually utilized for melting metals (Day, 1963). Since they are all chargeable to chemical react by the molten oxides, unfortunately, they cannot apply as a part to contact directly to the oxides melt (Klimm and Schroder, 1999). The high melting point metal such as molybdenum (T_m=2896 K) and tungsten (T_m= 3680 K) are oxidized rapidly by oxygen at high temperatures and can only be used in reducing or neutral atmospheres (Klimm et al., 2008b).

This chapter is organized as follows. An outline of thermodynamic background is illustrated in section 2. Section 3 contains a detailed discussion of the thermodynamic behaviour of construction materials (crucible, seed holder, after heater). Section 4 describes partial pressures effect of gases atmosphere. The short review of growth atmosphere effect on crystal growth process including two examples is presented in section 5. Section 6 concludes the chapter.

2. Thermodynamic background

Consider the general redox equilibrium reaction

$$aM_xO_y \leftrightarrow bM_zO_w + 1/2O_2 \tag{1}$$

With

$$\text{Log}\left(K_p\right) = \frac{1}{2.30R}(\Delta S^o - \frac{\Delta H^o}{T})(J.K^{-1}.mol^{-1}) \tag{2}$$

The equilibrium constant (K_p) gives the required combination of the activities of the reactants as

$$K_p = (\frac{a_{M_zO_w}^b \times P_{O_2}^{1/2}}{a_{M_xO_y}^a}) .$$

R is the universal gas constant, ΔH^o is the standard enthalpy change and ΔS^o is the standard entropy change for the reaction. The choice of the pure material a standard states makes the activity of material has values of unity in equation (2). In which case for material oxides, if the oxide pure is solid oxides, the activity of solid oxides will be unit. Moreover, when the material oxides would be gas forms the activity of the oxides replace to their pressures (Gaskell, 2003).

For the oxidation of (a)dn mole material oxide from the m valent state to the m- s valent state proceeds under the consumption of (s/2)dn mole oxygen. Herein m=2y/x and s=2/ax. m valent gives a number between 1-8 and always $m \geq s$. The Table 1 indicates four possible conditions of the redox equilibrium reactions which are obtained with simplifying the equation (1).

m	s	The redox equilibrium reaction
even	even	$2MO_{(m/2)} \leftrightarrow 2MO_{(m-s)/2} + \dfrac{s}{2}O_2$
even	odd	$2MO_{(m/2)} \leftrightarrow M_2O_{(m-s)} + \dfrac{s}{2}O_2$
odd	even	$M_2O_m \leftrightarrow M_2O_{(m-s)} + \dfrac{s}{2}O_2$
odd	odd	$M_2O_m \leftrightarrow 2MO_{(m-s)/2} + \dfrac{s}{2}O_2$

Table 1. The different conditions of redox equilibrium reaction.

The reaction equilibrium between pure material M, its oxide and oxygen gas where m=s would take place. In which case ΔG° is a linear function of temperature and a plot of ΔG°=RT Log (PO₂) versus temperature gives the lines for each oxidation reaction on an Ellingham diagram (Elingham, 1944). These lines separate phase regions where one oxidation state overcomes and the whole graph represents a predominance phase diagram for the material M and its oxides.

3. Construction materials

Platinum group metals and their alloys can usually be safely heated for long periods in contact with the more refractory oxides without serious risk of contamination. Due to their excellent chemical stability, oxidation resistance, and resistance to the action of many molten oxides, the platinum group metals: iridium, platinum and rhodium are widely used for high-temperature applications involving simultaneous chemical attack and mechanical strength. Important applications of platinum group metals are as crucibles for oxides crystal growth from melt. Oxides of major optical interest and their most suitable crucible materials are listed in Table 2.

Material	Oxide melting point (K)	Crucible	Material use
Lithium Niobate ($LiNbO_3$)	1523	Platinum or rhodium-platinum	Electro-optic
Calcium Tungstate ($CaWO_4$)	1839	Rhodium	Laser host
Gadolinium Gallium Garnet ($Gd_3Ga_5O_{12}$)	2023	Iridium	Laser host
Zinc Oxide (ZnO)	2248	Iridium	Green laser-UV light emitters
Sapphire (Al_2O_3)	2327	Iridium	Laser host

Table 2. Application of oxides single crystal and appropriate crucibles.

3.1 Platinum

The only materials that have been found to withstand high temperature chemical stability, oxidation resistance and resistance to react with many molten oxides are the platinum group of metals and their alloys. Although growth from Platinum crucibles can be performed in air, platinum does not appear to be widely used for the growth of oxide materials, probably due to its relatively low melting point (2042 K) in comparison to that for most refractory oxides or mixtures of oxides. The low melting point of lithium niobate ($LiNbO_3$), T_m=1523 K, (Day, 1963) and the chemical inertness of platinum suggested that this metal might be a useful crucible material, while platinum also offered some advantage in cost over the platinum group metals.

3.2 Rhodium

In a few instances, unalloyed platinum crucibles have been found satisfactory, but generally, it is necessary to choose materials of higher melting point, such as the rhodium platinum alloys, or the metals rhodium or iridium.

In the past, there has been some hesitation in the use of rhodium and iridium crucibles in oxidizing atmospheres at high temperatures through fear of high losses from the formation of volatile rhodium and iridium oxides. Based on this concept, Nassau and Broyer (1962) have used rhodium and iridium crucibles successfully for growing barium titanate single crystals. They were grown at about 1920 K from rhodium crucibles, when 0.36 weight percent of rhodium was detected in the crystals and from iridium crucibles when 0.02 weight percent of iridium was observed.

It is known that Rh reacts with oxygen above 1000 K (Chaston, 1965) forming Rh_2O_3 (s). Fig. 1 shows the stability regions phase in the Rh-O system from available thermodynamic data (Binnewies and Milke, 2008). As illustrated in Fig. 1, Rh_2O_3 (s) is stable up to 1412 K where the oxygen pressure reaches 1.0 atm. Above this temperature, Rh_2O_3 (s) decomposes to gaseous phase according to the equation

$$Rh_2O_3 \text{ (s)} = RhO_2 \text{ (g)} + 1/2O_2 \tag{3}$$
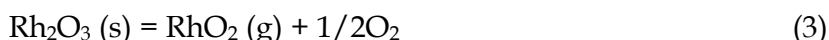
As pointed out, the dissociation of Rh_2O_3 at very low oxygen pressure $PO_2 < 10^{-35}$ (atm) and at room temperature, it maybe possible to take place this reaction

$$Rh_2O_3 \text{ (s)} = Rh \text{ (s)} + 3/2O_2 \tag{4}$$

From Fig. 1, it is limited to apply rhodium at high oxygen pressure as crucible because of evaporate to RhO_2. Therefore, the oxygen partial pressure must be low to avoid oxidation of crucible especially at low temperature.

3.3 Iridium

Owing to have a high melting point and high mechanical strength even at T> 2250 K°, iridium is a particularly suitable material for applications such as the stress-rupture strength, creep behavior and thermal shock which preclude the use of platinum alloys or rhodium (Weiland et al., 2006). Important applications of iridium is as crucible for pulling refractory oxides crystals such as GGG (T_m=2023 K) and ZnO (T_m=2248 K).

It is noticeable that iridium crucible are sensitive to oxygen, especially at the medium temperature (~870-1000 K°) as the metal would oxidize to solid iridium oxide. IrO_2 (s) decomposes to iridium metal at temperature higher than 1370 K° according to the equation

$$IrO_2 (s) = Ir (s) + O_2 \tag{5}$$

As illustrated in Fig. 2, IrO_2 (s) is stable at the temperature less than 1370 K^o at standard condition. If oxygen were applied at higher temperature than 1370 K^o, iridium parts would not be oxidized.
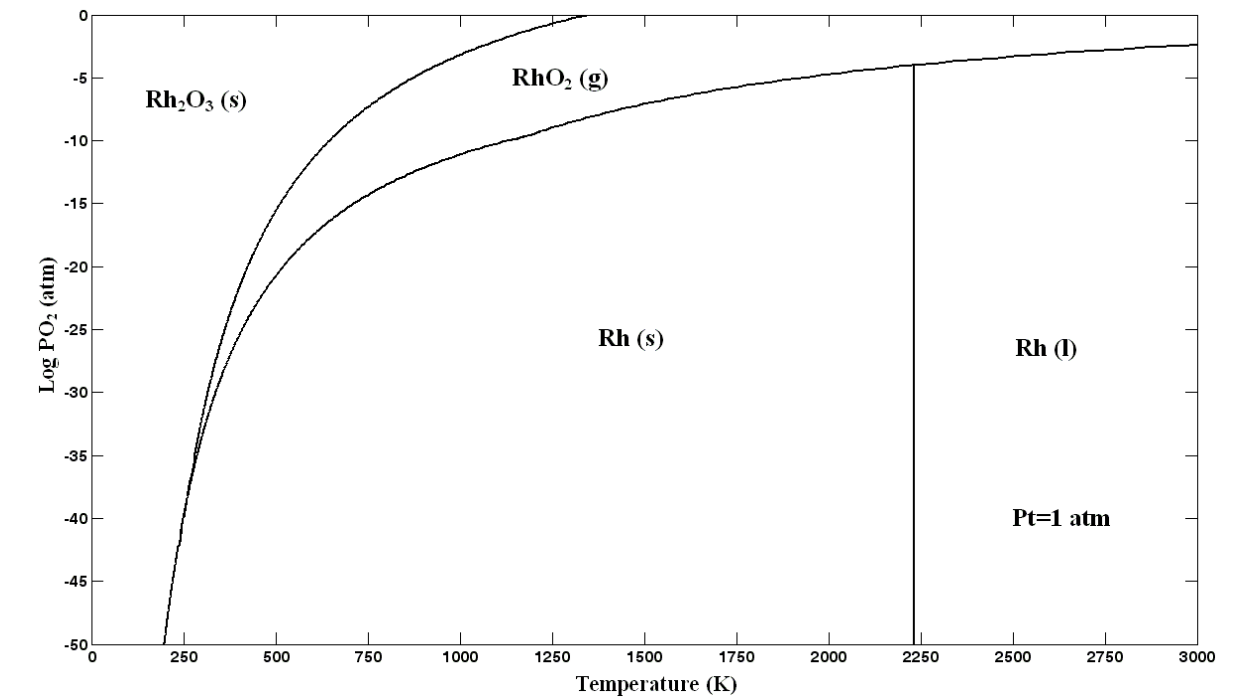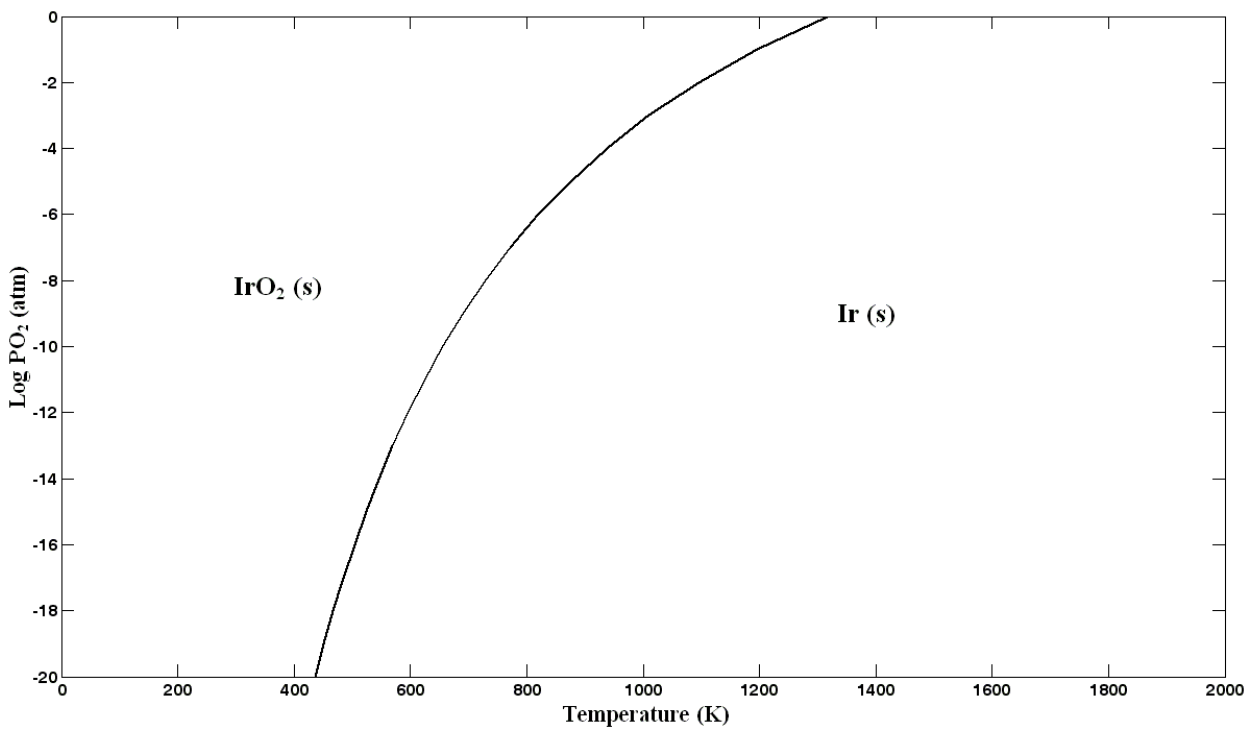

Fig. 1. Predominance diagram for Rh-O$_2$ system.

Fig. 2. Predominance diagram for Ir and IrO$_2$ (s) in the temperature- PO2 plane.

Several studies (Cordfunke and Mayer, 1962; Schafer and Heitland, 1960) have been shown that the oxidation of iridium at high oxygen pressure forms IrO_3 (g). As mentioned before, the decomposition temperature of IrO_2 (s) in oxygen at 1 atm is about 1370 K. Hence, above this temperature the equilibrium forming IrO_3 (g) follows

$$2Ir\ (s) + 3O_2 = 2IrO_3\ (g) \qquad (6)$$

Below 1370 K the volatile oxide dissociates to IrO_2 (s) and oxygen by the reaction (Cordfunke and Meyer, 1962)

$$2IrO_3\ (g) = 2IrO_2\ (s) + O_2 \qquad (7)$$

The major volatile species in the iridium-oxygen system is IrO_2 (g) (Chandrasekharaiah et al., 1981; Carpenter, 1989). For the reaction

$$Ir\ (s) + O_2 = IrO_2\ (g) \qquad (8)$$

The results of these thermodynamics calculation are plotted in Fig. 3 as Log PO_2 against temperature. It can be seen that IrO_3 (g) is identified as the major gaseous species at low temperatures (800 K- 1700 K). At 2033 K, Norman et al. (1965) determined the IrO_2 (g) pressure to be 1.9×10^{-8} atm and the IrO_3 (g) pressure to be 3.1×10^{-9} atm. This is indicated that at elevated temperatures IrO_2 (g) is predominant gaseous species (seen Fig. 3).
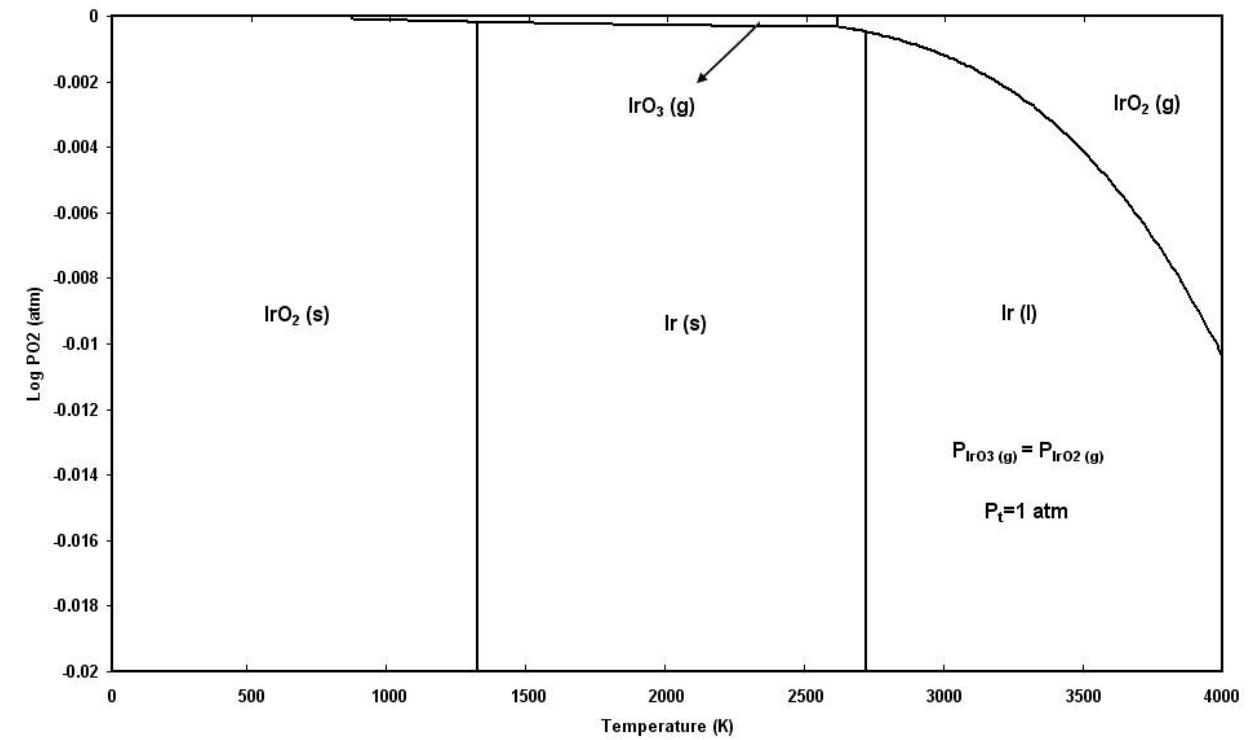

Fig. 3. Predominance diagram for Ir-O_2 system.

To sum up, although iridium is more sensitive to oxidation than platinum (E= -0.1474 V for Ir and E= -0.4422 V for Pt (Klimm et al., 2008c), it is the most chemically resistant of all metals. The high melting point of iridium (2716 K) and its resistance to attack by stable

oxide melts is maintained up to temperatures above 2250 K make it a particularly suitable material for oxides crystal growth from hot melt which preclude the use of platinum alloys or rhodium.

4. Growth atmosphere

The oxides crystal growth atmosphere should have two conditions
1) Consider a type of oxide material Me, in Table 1, i. e.,

$$Me_2O_m(s,l) \leftrightarrow Me_2O_{(m-s)}(s,l,g) + \frac{s}{2}O_2 \tag{9}$$
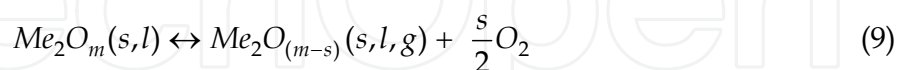
The oxygen partial pressure must be in that range where the favored valency of the oxide material (Me_2O_m) is stable. Always PO_2 system should be more than $(PO_2)_{min}$ to suppress the decomposition of oxide. Herein $(PO_2)_{min}$ is the minimum partial pressure of O_2 where the reaction (9) moves to the left side for the given growth temperature ($(PO_2)_{eq} > (PO_2)_{min}$).
2) For the reaction equilibrium between a pure solid construction material M, its pure oxide and oxygen gas

$$2M(s) + \frac{m}{2}O_2 \leftrightarrow 2MO_{(m/2)}(s, g) \tag{10}$$
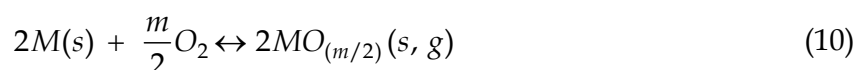
The oxygen partial pressure should be low enough to avoid oxidation of construction parts (crucible, seed holder) being in contact with the melt. Herein PO_2 system should be less than $(PO_2)_{max}$ with $(PO_2)_{max}$ - the maximum oxygen partial pressure where the construction material is equilibrium with its oxide in the m valency state ($(PO_2)_{max} > (PO_2)_{eq}$). Because the oxide construction parts are often stable at lower temperatures and oxide crystal almost decomposed at higher temperatures, both conditions are accomplished, if $(PO_2)_{min} < (PO_2)_{eq} < (PO_2)_{max}$. Commonly, amounts of oxygen, e.g. for the growth of $Gd_3Ga_5O_{12}$ (GGG) is about 1-2 vol% (Ganschow, 2010), add to the growth atmosphere to prevent volatile oxide. However, this value (PO_2) often is more than $(PO_2)_{max}$ at lower temperatures. Therefore, it causes that the construction material oxidized.
A solution to this problem is that mixtures containing an oxygen bearing gas like CO_2 or H_2O would be utilized in the growth atmosphere. They produce a temperature dependent oxygen partial pressure in this manner that the O_2 partial pressure increases with temperature. Hence, oxidation of construction parts decrease.
Another solution is that the protective gas (N_2, Ar) atmosphere would be charged into the furnace chamber in ambient temperature before heating the raw material and beginning the crystal growth process. The atmospheric pressure of the chamber should be more than ambient pressure. To prevent the evaporation of oxide, amount of oxygen should add into the during the crystal growth process at temperatures higher than temperature $MO_{m/2}$ decomposition. Growth experiments for Nd:GGG (Asadian, 2011) prove that the iridium crucible is not oxidized when the required oxygen was charged at T>1370 K°.

4.1 CO_2-CO system
CO_2 decomposes into CO and oxygen with increasing temperature according to

$$2CO_2 = 2CO + O_2 \tag{11}$$

If a moles of CO and 1 mole of CO_2 are mixed (a=CO/CO_2), then from stochiometry of Eq. (11), 2x moles of CO_2 would decompose to form 2x moles of CO and x moles of O_2 such that, at total pressure P_t, the PO_2 in CO-CO_2 system in various temperatures would be

$$Log \frac{x(a+2x)^2}{(1+a+x)(1-2x)^2}P_t = 9.04 - \frac{29613.35}{T} \tag{12}$$

Which,

$$PO_2 = \frac{x}{1+a+x}P_t \tag{13}$$

The partial pressure of oxygen can be "automatically" increased in the heating-up phase of the growth process by the thermal decomposition of carbon dioxide Eq. (11). Temperature dependence of PO_2 with comparing different gases for the above reaction is shown in Fig. 4.
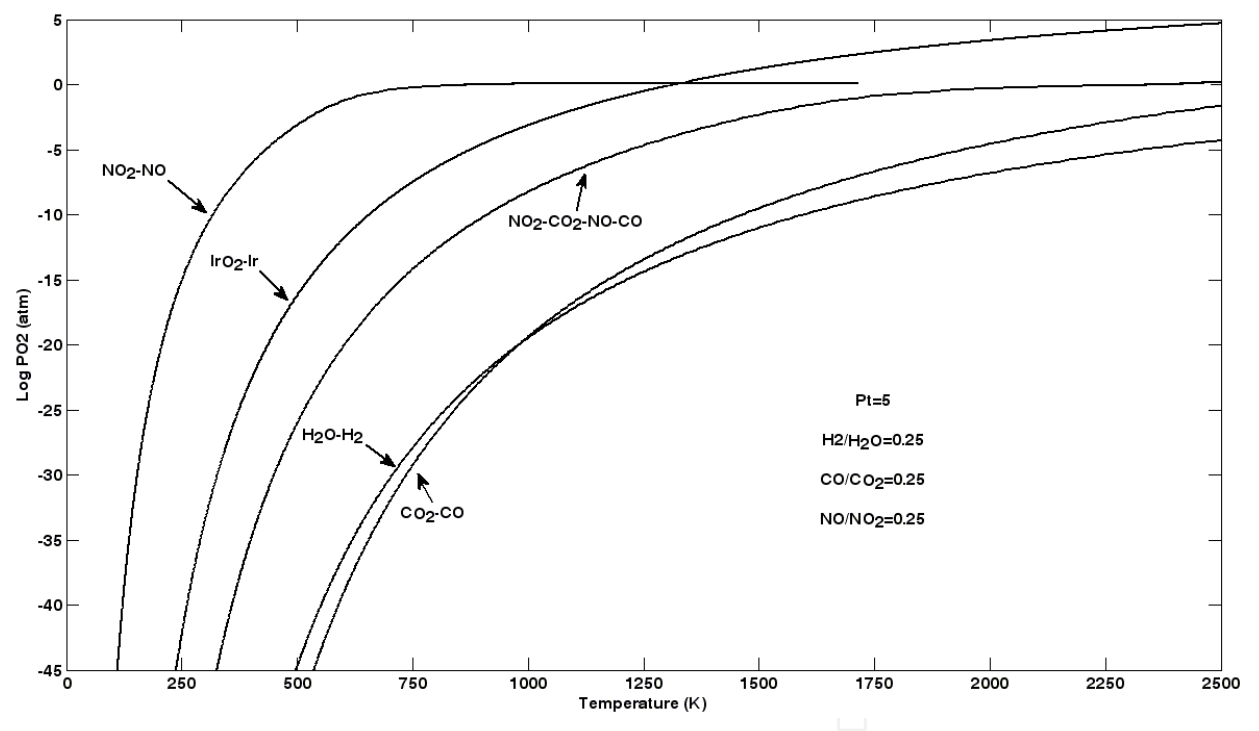

Fig. 4. Temperature dependence of PO_2 within different gases and gas mixtures comparing with stability regions for iridium (iridium metal and its solid oxide).

Thermodynamic calculations (Tomm et al.,2000) of the chemical equilibria between Ga_2O_3 (solid and liquid phase) and the surrounding gas-phase showed that an Ar+10% CO_2 atmosphere delivers an oxygen partial pressure that increases in such a manner with temperature, that Ga_2O_3 crystals can be grown from the melt. This amount of liberated oxygen is just sufficient to decrease the evaporation of molten Ga_2O_3 as well as low enough to allow the use of iridium crucibles, i.e., allowing Czochralski growth of Ga_2O_3.

4.2 H_2O-H_2 system

H_2O-H_2 system are used when it is required that the partial pressure of oxygen in a gas phase be fixed at a very low value at low temperatures. For example, if it were required to have a gaseous atmosphere containing an oxygen partial pressure of 10^{-30} atm at 705 K, then such an oxygen potential pressure can be obtained with simple relation by establishing the equilibrium

$$2H_2O = 2H_2 + O_2 \tag{14}$$

The partial pressure of oxygen in H_2-H_2O gaseous atmosphere in various temperatures from Eq. (14)

$$Log\frac{x(c+2x)^2}{(1+c+x)(1-2x)^2}P_t = 4.56 - \frac{25302.15}{T} \tag{15}$$

Which,

$$C = H_2/H_2O$$

$$PO_2 = \frac{x}{1+c+x}P_t \tag{16}$$

The oxygen pressure of H_2-H_2O is shown in Fig. 4. Comparing the H_2-H_2O system with CO-CO_2 indicate that H_2-H_2O system products more oxygen at lower temperatures. However, at higher temperatures CO-CO_2 system is the more efficient oxidant agent.

4.3 NO_2-NO system

Similarly, the partial pressure of oxygen in NO_2-NO system can be determined by establishing the reaction

$$2NO_2 = 2NO + O_2 \tag{17}$$

Thus

$$Log\frac{x(b+2x)^2}{(1+b+x)(1-2x)^2}P_t = 7.67 - \frac{5985.45}{T} \tag{18}$$

Which,

$$b = NO/NO_2$$

$$PO_2 = \frac{x}{1+b+x}P_t \tag{19}$$

The oxygen partial pressure in NO_2-NO gaseous atmosphere in various temperatures is drawn in Fig. 4. Comparing with others gaseous components, at lower temperatures the released oxygen is too much in NO_2-NO system. Therefore, the iridium crucible indeed would be oxidized.

4.4 NO$_2$-CO$_2$-CO-NO system

Consider the reaction CO$_2$ and NO$_2$ are mixed in the molar ratio 1:1 to form NO, CO and O$_2$ according to

$$CO_2 + NO_2 = CO + NO + O_2 \tag{20}$$

To obtain this gas mixture, CO$_2$ and CO, NO$_2$ and NO at total pressure P$_t$, would be mixed in the molar ratio CO/CO$_2$=a, NO/NO$_2$=b and allowed to equilibrate.
Which,

$$Log \frac{x(a+x)(b+x)}{(2+a+b+x)(1-x)^2}P_t = 8.36 - \frac{17799.40}{T} \tag{21}$$

$$PO_2 = \frac{x}{2+a+b+x}P_t \tag{22}$$

According Fig. 4, NO$_2$-NO and CO$_2$-CO gas mixtures can be used when it is required that the partial pressure of oxygen very low at lowers temperature to suppress oxidation of iridium crucible. Also they can be utilized when it is required that the high partial pressure of oxygen at elevated temperature. In this case, ZnO crystal growth is a good example. For the growth of ZnO in iridium crucible by Czochralski method, the oxygen partial pressure of chamber at ZnO melting point (2248 K) should be more than (PO$_2$)$_{min}$=0.35 atm (Klimm et al. , 2009) to have ZnO melt. In order to suppress the oxidation of iridium crucible, the PO$_2$ of system should be less than (PO$_2$)$_{max}$. According Table 3, NO$_2$-NO and CO$_2$-CO gas mixtures can be used for ZnO crystal growth.

PO$_2$ (atm) ⟍ Temperature	(PO$_2$)$_{min}$ (Ga$_2$O$_3$)	(PO$_2$)$_{min}$ (ZnO)	H$_2$-H$_2$O (PO$_2$)$_{eq}$	CO-CO$_2$ (PO$_2$)$_{eq}$	NO-NO$_2$ (PO$_2$)$_{eq}$	CO$_2$-NO$_2$-CO-NO (PO$_2$)$_{eq}$	(PO$_2$)$_{max}$ (iridium)
900 K	7.94×10^{-38}	9.52×10^{-14}	5.6×10^{-23}	2.0×10^{-23}	1.06	6.3×10^{-11}	2.57×10^{-5}
(T$_m$(G$_2$O$_3$)) 2080 K	1.12×10^{-5}	1.53×10^{-2}	4.89×10^{-7}	1.01×10^{-4}	1.33	0.63	10^2 <
(T$_m$(ZnO)) 2248 K	------	7.76×10^{-2}	4.0×10^{-6}	1.20×10^{-3}	1.41	0.89	10^2 <

Table 3. Maximum, minimum and required PO$_2$ that is supplied by different gas mixtures at different temperatures.

5. Oxides crystal growth

Oxides crystal growth are often performed from melts contained in crucibles, e.g. by Czochralski or Bridgman technique. For oxide components, oxygen partial pressure during growth is one of the most important parameters to decide about success or failure of crystal growth process. Many oxides may be easily decomposed at high temperatures and low oxygen partial pressure. Therefore, oxides crystal growth is often carried out in a protective gas atmosphere such as Ar and N_2 to avoid the oxidization of crucibles and to minimize dissociation of oxide. An amount of oxygen partial pressure is always necessary to remain the stability of the oxide.

5.1 Ga$_2$O$_3$

The growth of GGG single crystal by the Czochralski method, in high-quality and large-sized is hard because of the dissociation of Ga_2O_3 (Luo et al. ,2005; Li et al. , 2007). At the T> 1500 K^o (Klimm et al., 2008), reduction to evaporate Ga_2O may occur, whereas, the serious evaporation of Ga_2O_3 takes place at high temperatures. Fig. 5 represents a schematic of the experimental setup employed for the Nd:GGG crystal growth.
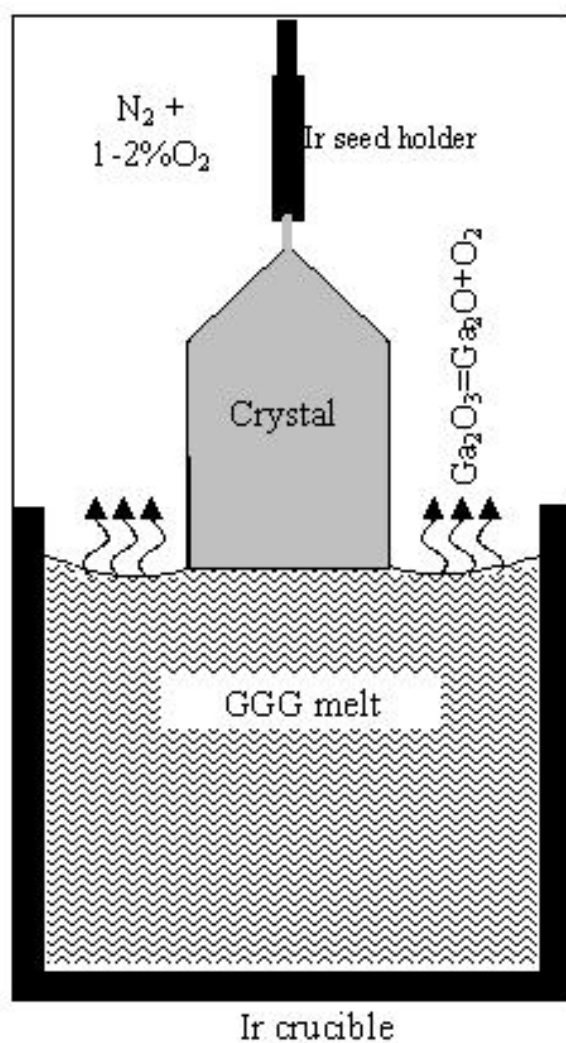
Fig. 5. Sketch diagram of GGG crystal growth setup.

Based on thermodynamic analysis, Ga_2O (g) and Ga (l) is main decomposed constituent via heating Ga_2O_3. During single crystal growth process by the Czochralski method, Ga_2O_3 sublimes by dissociation:

$$Ga_2O_3 \text{ (s,l)} = Ga_2O \text{ (g)} + O_2 \tag{23}$$

The diagram Log P_{O_2} (T) for gallium oxides is shown in Fig. 6. At above 1500 K$^{\circ}$, the evaporation of Ga_2O_3 may take place but the most serious Ga_2O_3 volatile will be happened at temperatures than higher 1950 K$^{\circ}$. According to the chemical equilibria law, charging amount of oxygen into system decreases the volatilization of Ga_2O_3. For GGG crystal growth by Czochralski method, the pressure of oxygen (PO$_2$) should be more than 10^{-4} atm to preserve stability of growth process.

Additionally, it would be extracted from Fig. 6, at lower pressures (PO$_2 < 10^{-11}$ atm), the decomposition of Ga_2O_3 to liquid gallium may occur.

$$Ga_2O_3 \text{ (s)} = 2Ga \text{ (l)} + 1.5O_2 \tag{24}$$

The liquid gallium will rapidly make to alloy with iridium crucible. Unfortunately, the formation of iridium-gallium alloys can definitely destroy the iridium crucible. Moreover, the Ga$^+$ ions decomposed from the Ga_2O_3 enter the lattice of Nd:GGG crystal ultimately cause the spiral growth.
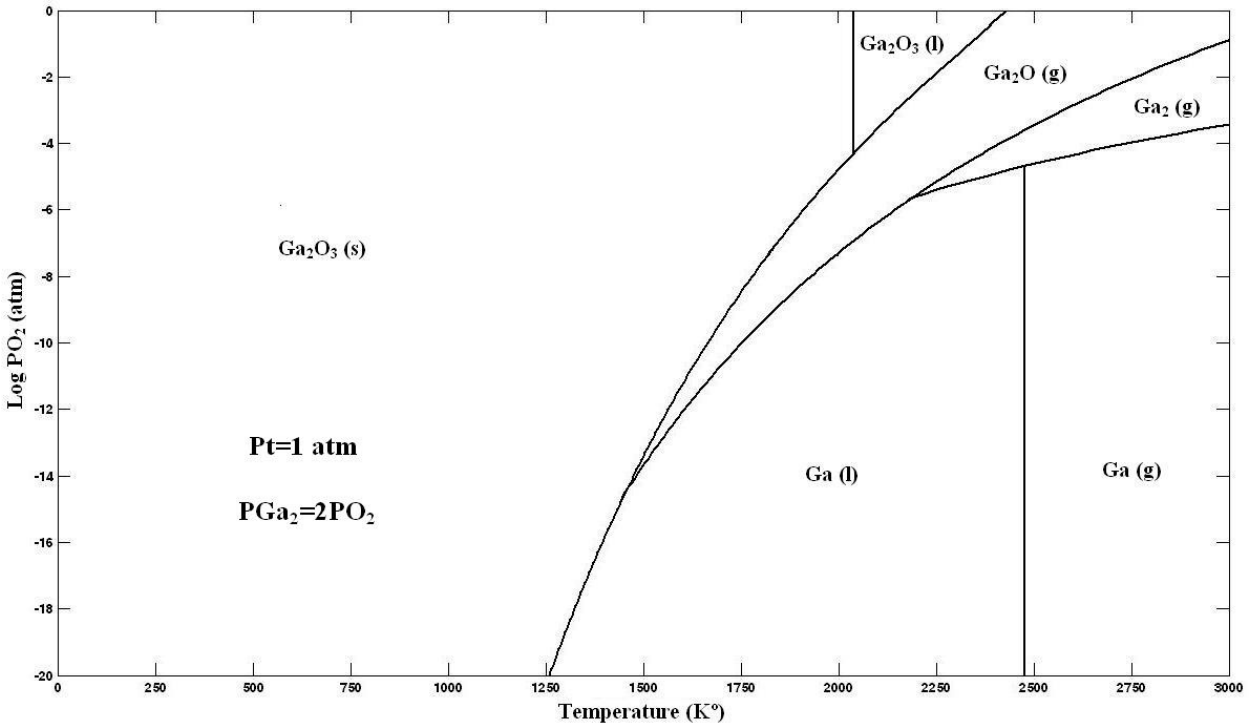

Fig. 6. Predominance diagram for Ga-O$_2$ system in dependence on T and the oxygen pressure PO$_2$ at total pressure 1 atm.

A solution to this problem is that the addition of oxygen would be replaced by carbon oxide (CO$_2$) in the growth atmosphere. The O$_2$ partial pressure increases with temperature; hence, oxidation of iridium crucible decreases (see Fig. 6). Matika et al. (1982) used a gas mixture of 50% CO$_2$ and 50% N$_2$ to reduce the dissociation of Ga_2O_3 and to suppress the formation of

iridium within crystals. They obtained the densities of dislocations and inclusions for single crystals were below 5 cm^{-2}. Tomm et al. (2000) reported the first successful growth of Ga_2O_3 single crystal by Czochralski method. They have decreased evaporation of molten Ga_2O_3 by means of Ar plus 10% CO_2 instead of O_2 in the atmosphere.

5.2 ZnO

Zinc oxide is a group II-VI semiconductor that most commonly exhibits wurtzite structure in its unstrained phase (Park et al., 2006). Wurtzite crystals can be cleaved cleanly along several different planes. The c-plane (0001) intercepts only the z axis and in the case of zinc oxide produces polar surfaces as a result of the lack of inversion symmetry along the c axis (Miller, 2008). Furthermore, because of its wurtzite crystal structure and lattice parameter (a=3.25A° in the a-direction) it is isomorphous with GaN and has potential as a substrate material for GaN-based epitaxial devices (Pearton, et al., 2005). It has a large exciton binding energy of 60 meV and, as a result, stimulated emission and lasing have been observed at room temperature (Bagnall et al., 1998)]. This means that ZnO excitons will remain bound at much higher temperatures than GaN and in doing so, offer the potential for greatly improved efficiency over GaN. This indicates that ZnO can be the preferred choice for future opto-electronic devices.

Attempts are made to grow ZnO a large number of different methods. Bulk ZnO crystals can be grown using melt (Klimm et al.,2008a), hydrothermal (Suscavage et al.,1999) and vapor phase growth techniques (Look et al., 2002).

Unfortunately, traces of the solvent are always incorporated in such hydrothermal crystals and hydrogen and lithium are found typically in concentrations of several 10^{18} cm^{-3}. In addition, the suitability of ZnO crystals for epitaxy is highly dependent on surface preparation and subsequent characterization.Therefore; Attempts have recently been made to grow single crystal bulk from the melt.

Single crystals of ZnO can be grown from the melt at high oxygen pressure and high temperature. The Czochralski (Klimm et al., 2008a) and Bridgman (Jacobs et al., 2009) methods are the most common melt-growth techniques used for production of the bulk single-crystal. The advantages of the Czochralski and Bridgman growth methods are relatively high growth rates (in the range of several millimeters per hour) and the nearly thermodynamically equilibrium conditions are capable to generate bulk crystals of high structural perfection. In addition, the doping techniques are well established in these two methods.

There are technical obstacles to the growth of single crystal ZnO from the melt. The triple point of ZnO (the temperature and pressure at which all three phases of that substance, gas, liquid and solid phases, coexist in thermodynamic equilibrium) is 2248 K under the total (Zn and O_2) vapor pressure of 1.06 atm.

Figs. 7 and 8 show the predominance diagram in the relevant temperature range of the Zn-O system at total pressures 1 and 5 atm, respectively. As it can be seen from Fig. 7, before the melting point, ZnO evaporates under dissociation

$$ZnO \ (s) = Zn \ (g) + 1/2O_2 \qquad (25)$$

It has strongly impeded the development of bulk crystal growth from the melt. To maintain the ZnO melt stable, the total pressure of oxygen-containing atmosphere in the growth chamber must be considerably larger than 1.06 atm.
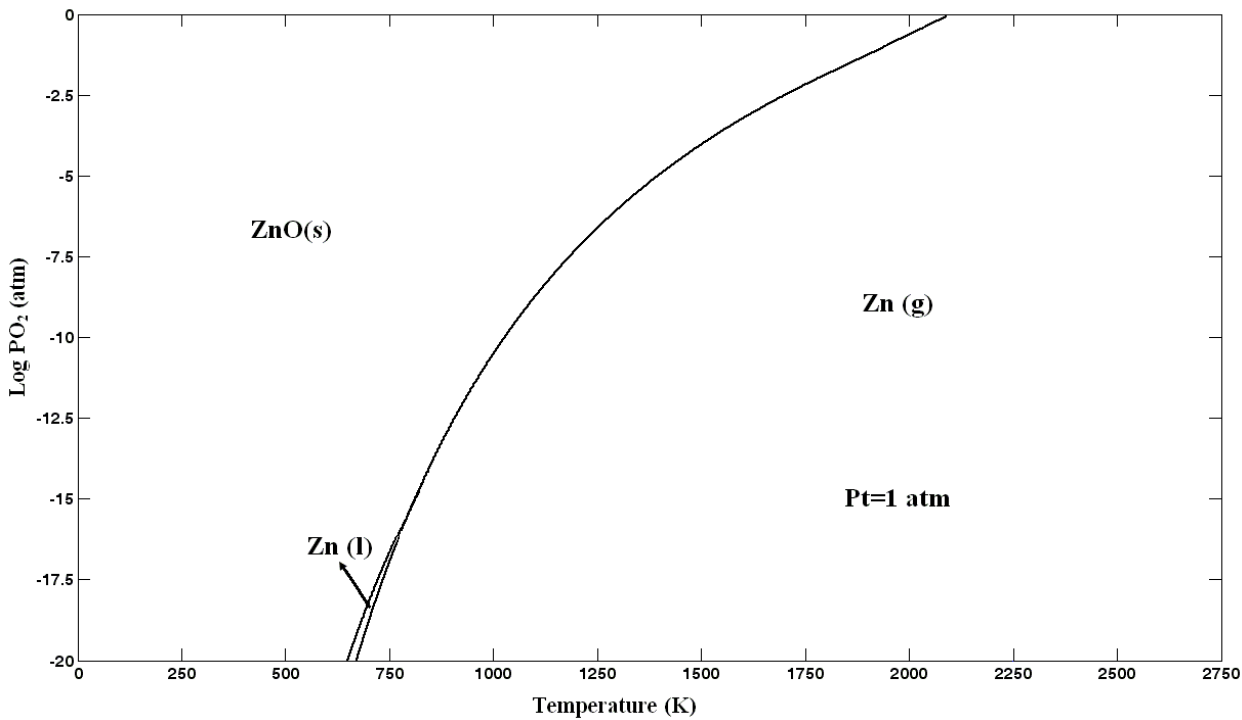
Fig. 7. Predominance diagram for Zn-O$_2$ system in dependence on temperature and the oxygen pressure PO$_2$ at total pressure 1 atm.
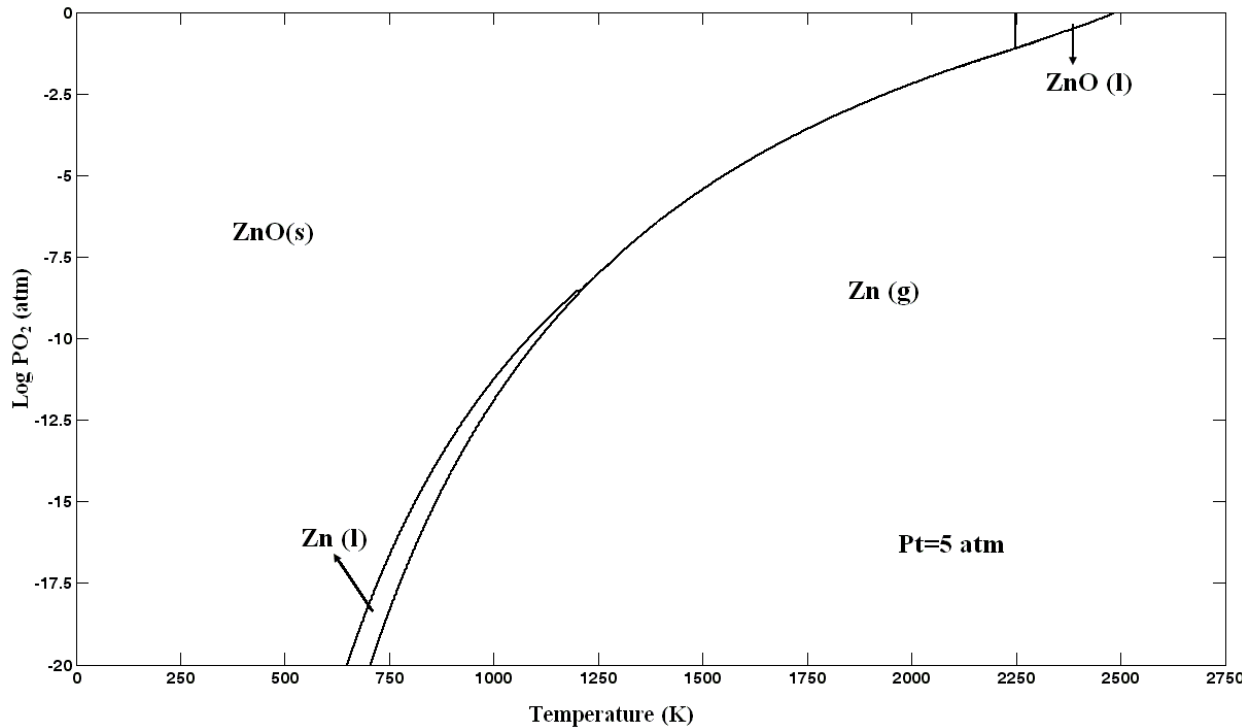

Fig. 8. Predominance diagram for Zn-O$_2$ system in dependence on temperature and the oxygen pressure PO$_2$ at total pressure 5 atm.

However, an essential difficulty to overcome is the lack of a perfect crucible material. The only metal withstanding high temperatures and an oxidizing atmosphere appears to be iridium. The design of a crucible containing molten ZnO capable of withstanding highly oxidizing conditions (temperatures of about 2300 K in oxygen containing atmosphere) is a serious challenge. The growth of ZnO crystals from a melt contained in an iridium crucible is continuously investigated by several references (Klimm et al., 2008a; Jacobs et al., 2009).

Indeed, it is well known that an atmosphere where iridium parts are to be heated must not contain more than 1-2% O_2 to avoid oxidizing of the metal. A solution could be try to heat the growth set up in the protective gas (N_2, Ar) –like GGG crystal growth- with an oxygen free atmosphere to 1000-1400 K and to add O_2 later, but practically this is not a solution for the problem. Although iridium crucible would not oxidize when the required oxygen was charged at T>1370 K°, crystal growth process would not stable growth because of sublimation of zinc oxide.

Similar problems during the melt growth of Ga_2O_3 were solved by working in a CO/CO_2 gas mixture. CO_2 yields an oxygen partial pressure well inside that corridor. At low temperatures, equilibrium reaction (11) is far on the left side and the oxygen partial pressure is very low. With increasing temperature, the equilibrium is shifted more and more to the right side and the resulting oxygen partial pressure is represented by curve in Fig. 9. Using CO_2 at a total pressure of approximately 10 bars, the authors (Klimm et al., 2008a; Klimm et al., 2008c; Jacobs et al., 2009) have successfully grown ZnO crystals from the melt in a Bridgman-like configuration.
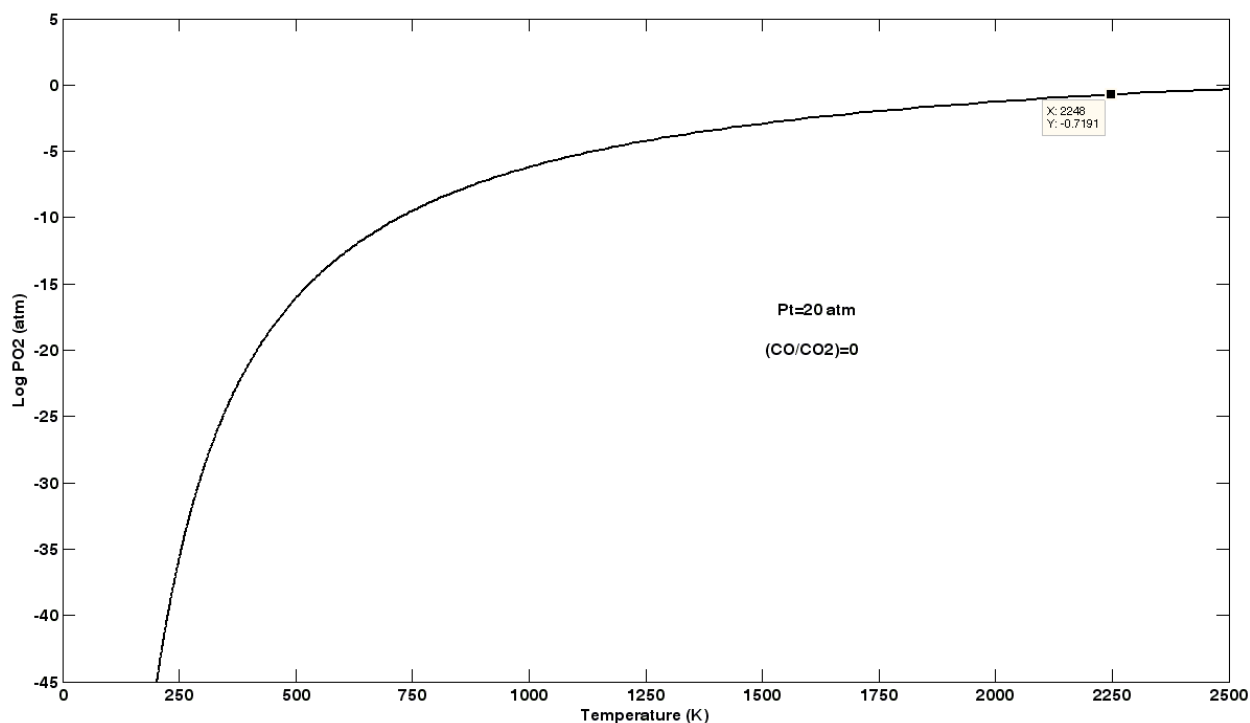

Fig. 9. The Oxygen partial pressure of pure CO_2 is against temperature at total pressure 20 atm.

The researches on growth of ZnO single crystals by the Czochralski method were carried on until now. Unfortunately, all attempts to obtain crystallization of bulk ZnO failed. Only polycrystalline ZnO solidified on the iridium seed rod was reported (Klimm et al., 2008a).

The control of the Czochralski experiments failed as the evaporation rate of ZnO at the melting point is high, even under the pressures up to 20 atm that were used. However, the partial pressure of O_2 at total pressure 20 atm that is supplied by pure CO_2 barely reaches to 1.90×10^{-1} atm at the melting point of ZnO crystal (seen Fig. 9). As shown in Fig. 10, the evaporated material forms white fume laying above the melts surface making optical control of the seeding process almost impossible (Klimm et al., 2008a). Moreover, evaporated ZnO condenses partially on the iridium seed rod, especially where it is lead through the thermal insulation. The sublimate creates mechanical contact between both parts, thus hindering mass control of the crystallizing ZnO by the balance on top of the seed rod that would otherwise allow automatic diameter control of the Czochralski growth process.
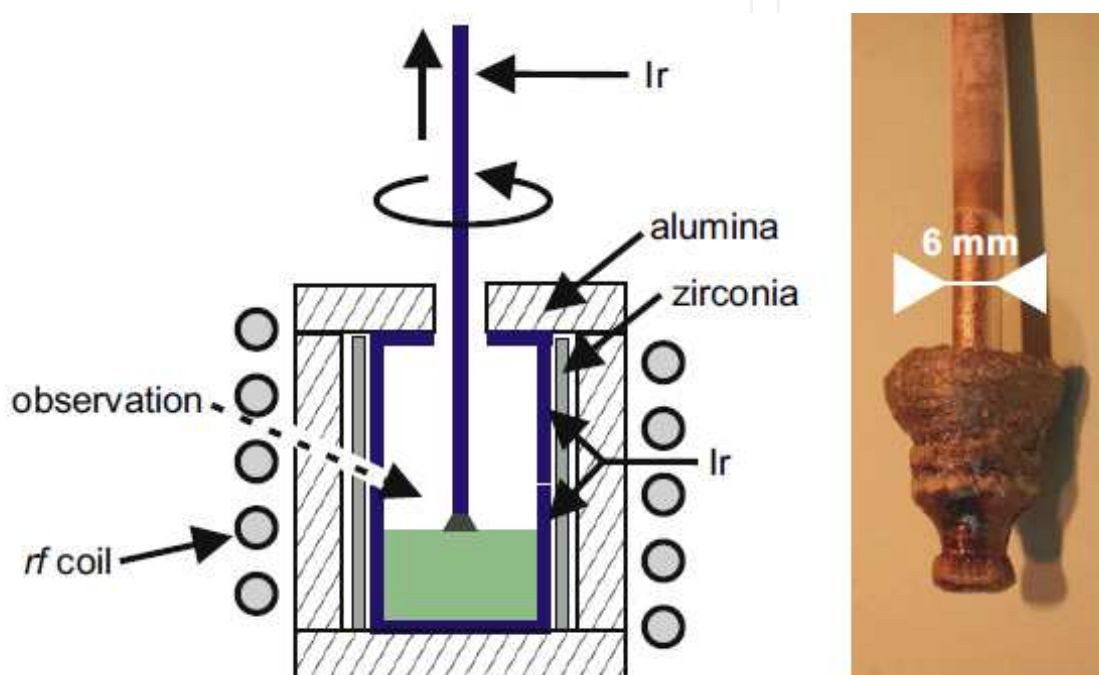
Fig. 10. Left: A schematic illustration of the ZnO crystal growth apparatus,
Right: polycrystalline ZnO solidified on the iridium seed rod. (Klimm et al., 2008a)

The Table 3 shows that at T_m=2248 K (melting point of ZnO), the pressure of oxygen at total pressure 5 atm should be between $(PO_2)_{min}$ and $(PO_2)_{max}$ points ($-1.11 < \text{Log } PO_2 < 2$) in order to have growth stability and suppress the burning of the construction parts (crucible, seed holder). Based on Table 3, the oxygen partial pressure of gas mixtures containing (CO-NO-CO_2-NO_2) with (CO/CO_2)=0.25 and (NO/NO_2)=0.25 is reached to Log PO_2=-0.05 atm. Compared with NO-NO_2 system, It is not only placed among of $(PO_2)_{min}$ and $(PO_2)_{max}$ at the melting point of ZnO but also it is less than the partial pressure of oxygen at lower temperatures of 1370 K. Best of all, the ZnO crystal growth can be performed at lower total pressures (< 5 atm) compared with CO-CO_2 system (>20 atm).

6. Conclusion

During the growth of refractory oxides crystal from melt, appropriate partial pressure of O_2 in the chamber is needed to keep the growth process stable. On the other hand, the partial pressure of O_2 should be kept low adequate in lower temperatures to suppress the oxidation

of constructive parts specially crucible. The best solution to this problem is that the PO_2 that is supplied by–depends on thermodynamic behavior of oxide- pure CO_2 or by a mixture of CO-CO_2 or NO-CO-CO_2-NO_2 would be utilized in the growth atmosphere. They produce a temperature dependent oxygen partial pressure in this manner that the O_2 partial pressure increases with temperature. This amount of liberated oxygen is just sufficient to decrease the evaporation of molten oxides as well as low enough to allow the use of iridium crucibles, i.e., allowing Czochralski growth of Ga_2O_3 or ZnO.

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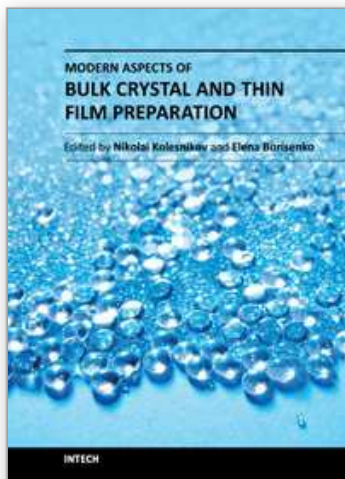
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