INTRODUCTORY NOTE: Defect corridor along the compensated furnace trajectory (CFT) in sapphire heat treatment

AUTHOR: Ted Themelis
AFFILIATION: Independent Researcher, Gemlab, Bangkok, Thailand
ORCID: 0000-0002-4493-6623
Email: ted@themelis.com

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Abstract
In this study the compensated furnace trajectory (CFT), established for the Lakmini LPG–O_2 combustion furnace is examined through a first-order defect framework. Point-defect equilibria in corundum are governed by oxygen chemical potential, with oxygen fugacity ($_fO_2$) acting as the thermodynamic proxy linking combustion compensation to defect tendencies. A schematic Brouwer-type diagram distinguishes oxidizing, intermediate (Bluing Window), and reducing regimes, where Fe^{2+} formation becomes progressively favored. Within the intermediate reduction interval, Fe^{2+}–Ti^{4+} intervalence charge transfer (IVCT) becomes thermodynamically accessible while oxygen-vacancy tendency remains limited, preserving lattice stability.

The reduction corridor is bounded by the Iron–Wüstite buffer (IW) and ilmenite-related (IRI) instability limits, beyond which precipitation reactions and lattice instability dominate. Experimental validation at 1650 °C identified a practical compensation interval centered near $\Phi_{CFT} \approx 0.88$, bounded by the Titration Point (TP) and Soot Disappearance Boundary (SDB). These defect tendencies become operationally relevant only after applying the dimensionless Furnace Indicator Factor Integration (FIFI), expressed as Φ_{CFT}. This parameter defines the compensated furnace trajectory at 1650 °C, establishing an operational thermochemical coordinate that links combustion control directly to defect accessibility in heated corundum.

1. Background

The Lakmini LPG–O_2 furnace exhibits structural combustion asymmetries that influence operational redox behavior. This study utilizes the Furnace Indicator Factor Integration (FIFI), a dimensionless coordinate introduced by the author *(Themelis 2026b)* and denoted as Φ_{CFT}. This parameter represents the normalized combustion state produced by LPG–O_2 adjustment and is experimentally bounded by the titration point (TP) and soot-disappearance boundary (SDB).

However, Φ_{CFT} remains a variable parameter because the compensation terms entering FIFI differ between furnaces, causing TP and SDB to shift as moving thermochemical pillars along the CFT. The present note examines the defect corridor of the compensated furnace trajectory in relation to oxygen fugacity ($_fO_2$) and the associated defect tendencies governing potential blue color development.

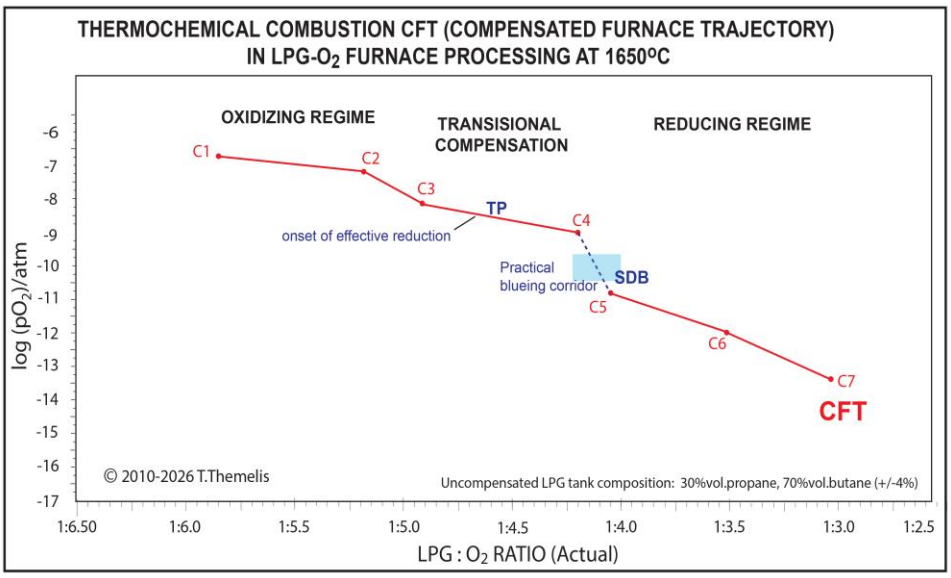

Figure 1. *Thermochemical compensated furnace trajectory (CFT) for the Lakmini LPG–O_2 furnace at 1650 °C. The shaded Practical Bluing Corridor corresponds experimentally to $\Phi_{CFT} \approx 0.88$, bounded by the Titration Point (TP) and the Soot Disappearance Boundary (SDB). Within this range, reduction becomes sufficient to favor Fe^{2+} formation while oxygen-vacancy tendency remains thermodynamically limited. This defines the Fe-controlled redox corridor within which Fe^{2+}–Ti^{4+} (IVCT) becomes thermodynamically accessible before entry into the destructive IW–IRI precipitation corridor.*

2. Defect interpretation of the CFT

Point-defect equilibria in

corundum are governed by oxygen chemical potential, whereby the CFT can be interpreted through a Brouwer-type framework using $_fO_2$ as the main thermodynamic variable. The Brouwer-type representation used here is schematic and expresses relative defect tendencies rather than calculated equilibrium concentrations or formal slope exponents.

Within this schematic treatment, ferric–ferrous iron is tracked as the primary oxygen-sensitive redox indicator, while titanium remains compositionally stationary within the host lattice, unplotted as an independent defect species, yet thermodynamically available for subsequent intervalence charge transfer (IVCT).

Oxidizing regime: Electronic holes (h•) dominate and ferric iron (Fe^{3+}) remains stabilized. Fe^{2+}–Ti^{4+} (IVCT) remains limited, resulting in weak potential for blue development.

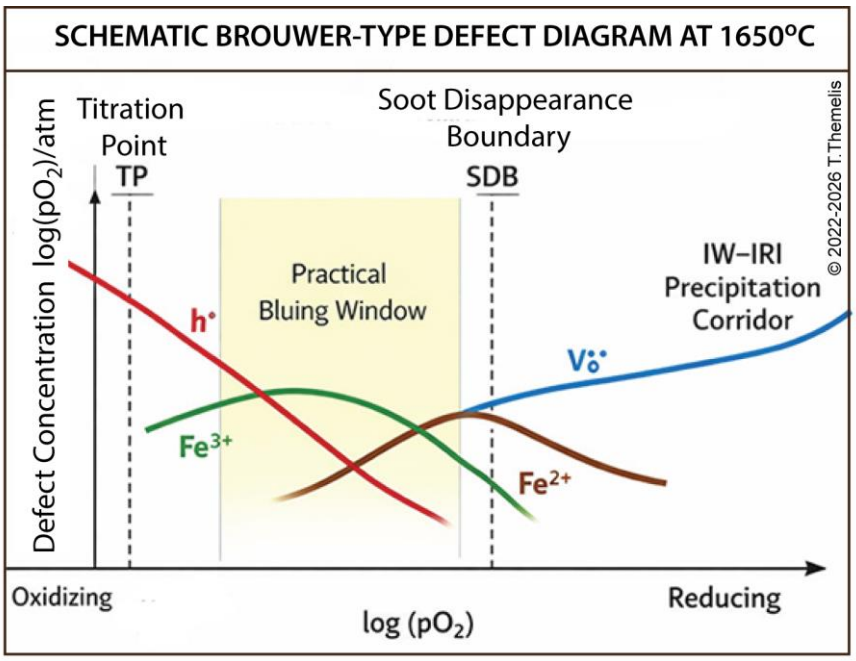

Figure 2. *Schematic Brouwer-type defect diagram at 1650 °C showing the Practical Bluing Window and the IW–IRI precipitation corridor. Lines are schematic and indicate relative defect tendencies only. Relative defect tendencies in corundum are shown as a function of decreasing oxygen fugacity ($_fO_2$) at 1650 °C, following the reducing progression associated with the compensated furnace trajectory (CFT). TP and SDB correspond approximately to $\Phi_{CFT} \approx 0.88$.*
The descending red line (h•) represents progressive annihilation of hole defects as reduction proceeds. The green line (Fe^{3+}) decreases as ferric iron is reduced, while the brown line (Fe^{2+}) rises correspondingly and intersects Fe^{3+} within the Practical Bluing Window before extending toward the IW–IRI precipitation corridor. This crossing marks the Fe-controlled redox interval within which Fe^{2+} becomes sufficiently available for local coupling with lattice-bound Ti^{4+} where impurity proximity permits Fe^{2+}–Ti^{4+} (IVCT). Beyond SDB, the blue line ($V_{O}^{\bullet\bullet}$) indicates increasing oxygen-vacancy tendency under stronger reduction, marking progressive approach toward the IW–IRI corridor where excessive reduction favors hercynite ($FeAl_2O_4$), ilmenite ($FeTiO_3$), and grey metallic clouding.

Practical Bluing Window: Defined by the interval between the Titration Point (TP) and Soot Disappearance Boundary (SDB). As oxygen potential decreases, mixed-valence Fe^{3+}–Fe^{2+} states emerge, activating a redox interval where Fe^{2+} becomes sufficiently available for local coupling with lattice-bound Ti^{4+}. Within this window, IVCT is favored where impurity proximity permits, without triggering excessive reduction or thermodynamic instability.

Reducing regime: The tendency for doubly charged oxygen vacancies ($V_{O}^{\bullet\bullet}$) increases alongside Fe^{2+} stabilization. While further reduction may initially intensify color, approaching the limits of thermodynamic stability triggers phase precipitation and lattice instability.

3. Practical reduction limits and instability boundaries
Thermodynamic limits are constrained by oxygen fugacity buffers, with the IW and ilmenite-related instability (IRI) buffers defining the lower reduction corridor. Crossing the IW boundary increasingly stabilizes ferrous iron (Fe^{2+}), promoting grey metallic clouding. Further reduction toward the IRI domain promotes Fe–Ti oxide precipitation and lattice instability, as illustrated in Figure 3, which defines the thermodynamic floor of the reduction corridor.

These dynamics explain recurrent failures — specifically grey clouding and white particulate inclusions — observed in both Lakmini and electric muffle tube furnaces in environments utilizing carbon- or hydrogen-based reductants such as LPG/Ar, H_2/Ar, CO/CO_2, H_2O/H_2, and related buffering systems. Experimental heating indicates phase instability onset near 1600 °C, where corundum frequently develops pearly textures and white specks attributed to hercynite formation.

Currently, 1650 °C represents the most effective practical operating compromise, balancing IVCT activation against precipitation risk. To avoid irreversible structural damage, reduction must remain thermodynamically constrained above the IW boundary.

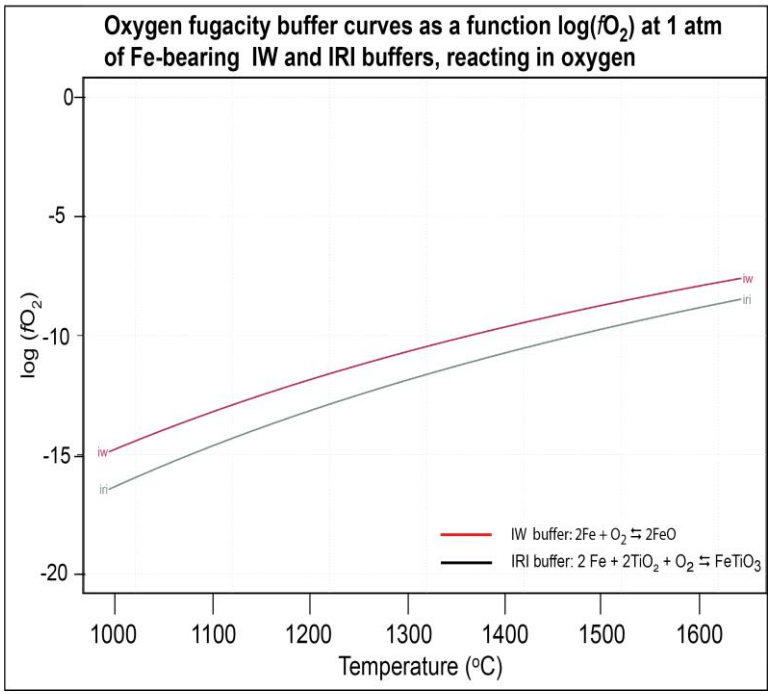

Figure 3. *Oxygen fugacity (fO_2) stability diagram defining the practical lower reduction corridor for corundum at elevated temperature. The thermodynamic interval above the IW buffer defines the practical lower reduction corridor where controlled blue development remains possible through Fe-controlled access to the mixed-valence interval required for Fe^{2+}–Ti^{4+} (IVCT) in corundum. Progressive reduction toward the ilmenite-related IRI boundary increases the likelihood of grey metallic clouding, hercynite ($FeAl_2O_4$) formation, and Fe–Ti oxide precipitation. Within the practical operating range at 1650 °C, this reduction interval corresponds approximately to $\Phi_{CFT} \approx 0.88$, bounded above by TP and below by SDB, beyond which thermodynamic instability increases rapidly.*

4. Practical implication

The scientific value of the compensated furnace trajectory lies in linking combustion compensation directly to solid-state defect evolution. It defines a narrow thermodynamic corridor in which blue development becomes accessible when reduction favors Fe^{2+}–Ti^{4+} (IVCT), while remaining sufficiently constrained to suppress destructive phase precipitation. This framework identifies Fe-controlled access to the mixed-valence interval rather than exhaustive impurity-pair kinetics.

These defect tendencies become operationally relevant only after Φ_{CFT} aligns the Lakmini furnace with the compensated trajectory. Under uncompensated operation, structural combustion asymmetries prevent stable thermochemical positioning. For practical sapphire heating, the operative compensation interval near $\Phi_{CFT} \approx 0.88$ defines the experimentally reproducible bounds of the redox corridor.

Navigating this interval permits the mixed-valence crossing required for coloration while avoiding irreversible reduction damage such as grey metallic clouding and hercynite precipitation. Within this range, ΦCFT functions as the practical thermochemical control coordinate linking combustion compensation to defect accessibility in heated corundum. This framework is intended as a thermochemical guide for locating the practical defect corridor rather than as a fully predictive defect model.

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