KROGER: An Extended Calculation Framework for Realistic Defect Modeling in Semiconductors

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Accurate defect modeling is essential for optimizing semiconductor materials for electronic applications. Here, we introduce KROGER [1], a robust computational framework that integrates density functional theory (DFT) with thermodynamic effects such as bandgap temperature dependence, chemical potentials, and defect vibrational entropy. KROGER enables precise predictions of defect equilibria, charge carrier compensation mechanisms, and kinetic trapping effects, providing valuable insights into material processing and defect engineering.

KROGER models full, partial, and constrained defect equilibria to capture the influence of growth and processing conditions on defect chemistry. Named after F.A. Kroger for his seminal work on point defect equilibria, KROGER processes large-scale datasets of DFT-computed formation energies for defects and complexes, allowing defect population predictions under real-world conditions. It accounts for self-trapped holes (STHs) and incorporates a quantum harmonic oscillator model to estimate defect vibrational entropy, which contributes energy corrections exceeding 1.5 eV per defect near the melting point.

To demonstrate its capabilities, we apply KROGER to β-Gallium Oxide (β-Ga_2O_3), an ultra-wide bandgap semiconductor with promising applications in power electronics. Accurate modeling of defects in β-Ga_2O_3 is crucial for optimizing its electrical properties and doping strategies. A key challenge in defect modeling is predicting defect concentrations under real-world synthesis conditions. Standard DFT-based formation energy calculations often predict full compensation of n-type doping by gallium vacancies (V_{Ga}), contradicting experimental findings. However, Sn-doped β-Ga_2O_3 crystals grown by edge-fed growth (EFG) at 2068°C with p_{O2} = 0.02 atm exhibit degenerate n-type conductivity with minimal compensation. By incorporating temperature-dependent bandgap corrections, realistic chemical potentials from the Ga-O binary phase diagram, and vibrational entropy effects, KROGER significantly improves agreement with experimental data.

In this study, we modeled 873 charge states of 259 defects, including native and impurity-related species involving 19 elements, to simulate the defect chemistry of β-Ga_2O_3 under EFG growth and oxygen annealing. KROGER accurately predicts unintentionally doped (UID), Sn-, Fe-, and Mg-doped EFG crystals by computing defect equilibria based on experimentally reported impurity concentrations. This approach provides insights into kinetic trapping mechanisms influencing dopant distributions and charge compensation. Additionally, we validate our results against deep-level optical spectroscopy (DLOS) data for V_{Ga}-related defects and experimental electron-donor concentration ratios in Sn-doped β-Ga_2O_3.

A key advancement is Sequential Quenching, bridging equilibrium and infinitely fast quenching models by incorporating defect-specific diffusion kinetics. This method allows semi-quantitative predictions of defect distributions in finite-sized samples subjected to realistic cooling rates. By freezing defects at distinct temperatures based on their diffusion constants, KROGER predicts spatial defect distributions across bulk crystals and thin films, enabling precise defect engineering strategies for optimizing material performance in power electronics.

This study highlights the necessity of integrating first-principles calculations with thermodynamic corrections to achieve predictive accuracy in defect modeling. KROGER provides a powerful and transferable framework for semiconductor defect engineering, setting a

benchmark for predictive modeling in electronic materials

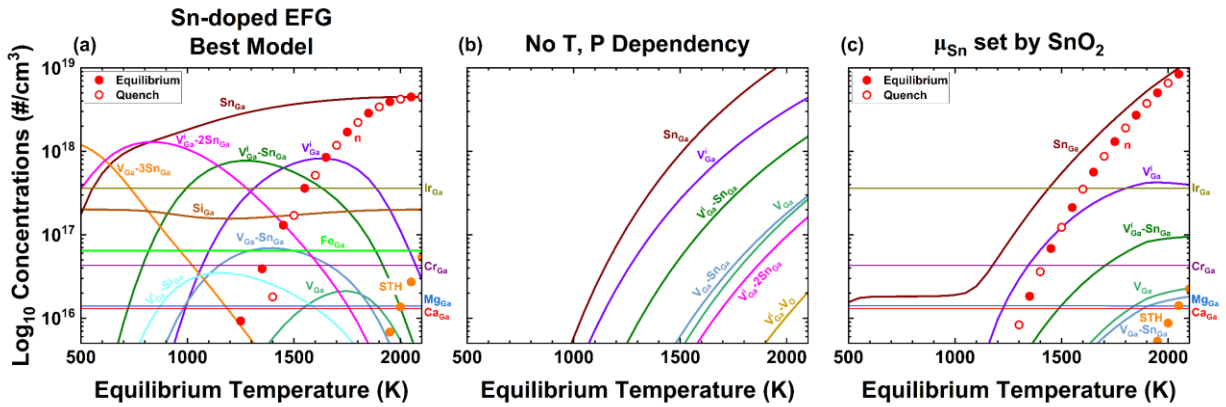

Fig. **1**. Defect Concentrations in Sn-Doped β-Ga_2O_3 Under Different Conditions. (a) Full temperature-dependent effects with fixed impurity concentrations at pO_2 = 0.02 atm, consistent with n-type conductivity and <1% compensation if native defects freeze-in by ~1950 K, (b) "O-rich, Sn-doped" conditions without temperature dependencies, incorrectly predicting insulating behavior with >99% compensation, (c) Sn solubility limited by equilibrium with SnO_2, requiring simultaneous freeze-in of native defects and Sn at ~1850 K, implying unlikely sensitivity to cooling rate. Evidence suggests kinetic trapping enables high [Sn] without SnO_2 precipitation.

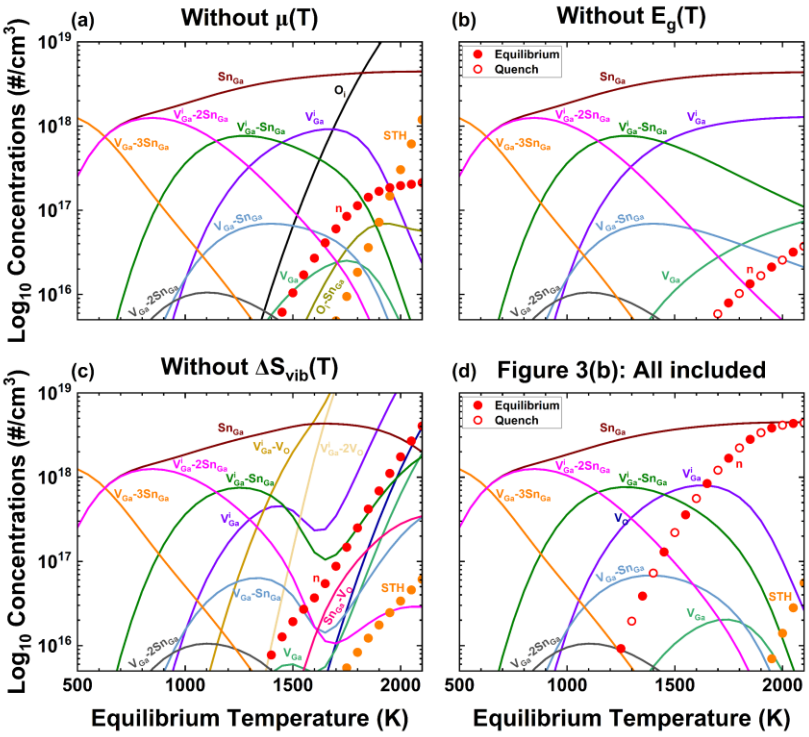

Fig. 2. Effects of omitting one temperature dependence at a time to investigate their importances. Conditions kept constant are [Sn]=4.5x10^{18} /cm^3 and f=0.40. (a) Adopting T-independent O-rich conditions as in Fig. 1(b) predicts O_i are the dominant compensating acceptors at high temperature and at no temperature does n=[Sn]. (b) Effect of E_g(T), N_C(T), and N_V(T) held constant at 300 K values, again there is no temperature where n=[Sn]. (c) Effect of omitting DS_{vib}(T) – here there is only one temperature at which n=[Sn] so coincidence would be required for agreement with experiments. Also, the concentrations of V_{Ga} and divacancy complexes increase to at% concentrations, which would be possible to measure. (d) Replication of Fig. 3(b) including all effects to facilitate side-by-side comparison.

[1] K. A. Arnab *et al.*, "Quantitative Modeling of Point Defects in $β$-Ga2O3 Combining Hybrid Functional Energetics with Semiconductor and Processes Thermodynamics,", *arXiv*: arXiv:2501.17373 (2025).