Supporting Information: Probing the Kinetics of Crystallite Growth in Sol-Gel Derived Metal-Oxides Using Nanocalorimetry

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This document contains additional information referred to in the main text. The content is organized into the following three sections:

- **Total Heat Flow**: An illustration of the total heat flows measured on each leg of the temperature-time profile defined in Figure 2.
- **Crystallite Growth as a Sequential Process**: Corroborating measurements in support of crystallite growth as a sequential, irreversible process that follows each decomposition temperature-time interval. Additionally, we show the consistency of the

measurement technique under repeated temperature-time cycling of a given nucleation and growth profile.

- **Extraction of Activation Energy**: Definition of the Ozawa and Kissinger methods of extracting the activation enthalpy of the crystallization process.

Total Measured Heat Flow

The total heat flow measured for each temperature segment corresponding to the temperature profile defined in Figure 2 is shown in Figure S1. It can be seen that there exists a distinct temperature region wherein crystallization (exothermic) peaks appear separate from decomposition (endothermic) peaks.

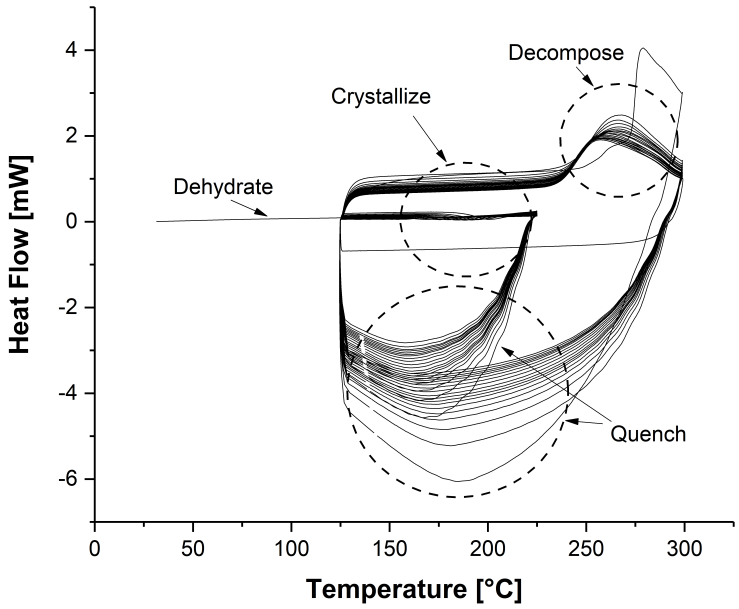

Figure S1: Measured heat flow as a function of temperature for different heating rates, corresponding to the temperature profile in Figure 2

Crystallite Growth as a Sequential Process

In Figure S2, the total heat flow signal is shown corresponding to one decomposition heating segment and repeated crystallization heating segments according to the profile shown in Figure 2. As shown, a single decomposition peak and crystallization peak appear, with unchanging subsequent scans. This indicates that the exothermic peaks we observe occur sequentially following a partial decomposition of the sample, consistent with theoretical expectations that crystallite growth occurs after nucleation.

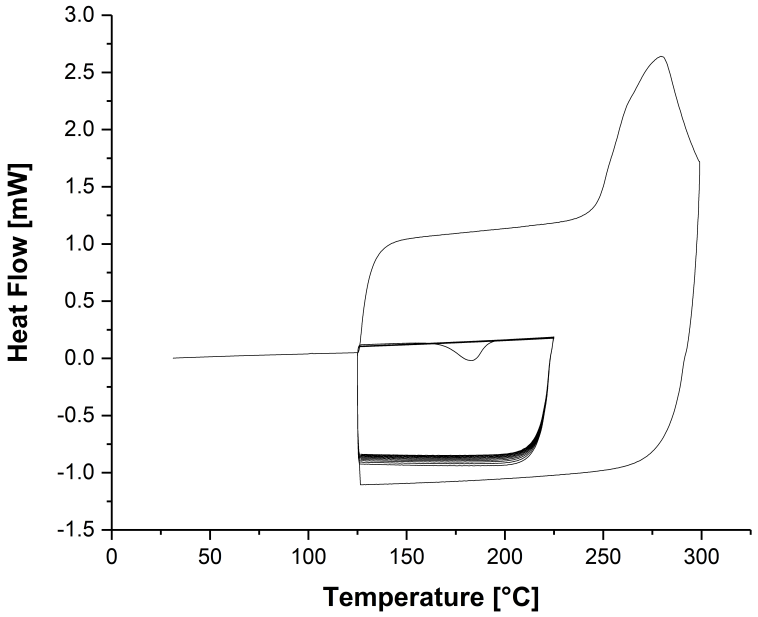

Figure S2: Result of applying a single heating cycle (Decomposition, quench, crystallize at $10\,^{\circ}\mathrm{C\,s^{-1}}$, quench) followed by subsequent heating cycles with the decomposition step removed (crystallize, quench). As shown, only a single crystallization peak is observed, indicating that the crystallite growth process necessarily follows decomposition.

Furthermore, the repeatability of a single temperature profile is assessed in Figure S3. Here, a temperature cycle is repeated for the same heating rate of $10\,^{\circ}\mathrm{C\,s^{-1}}$. From this data it can be inferred that the difference between exothermic events corresponding to repeated scans is much smaller than that corresponding to changes in the heating rate, which is the primary variable in our kinetic study of crystallite growth.

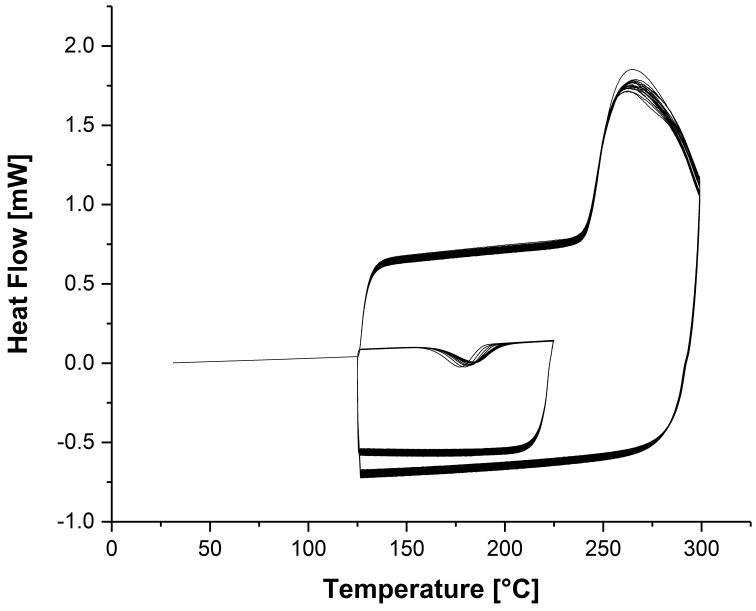

Figure S3: Results of applying the same heating profile shown in Figure 2 repeatedly to the same zinc acetate dihydrate sample. As shown, the measured heat flow is relatively consistent for each cycle as expected.

Extraction of Activation Energy

Figures S4 and S5 illustrate the data used for the extraction of activation energy of crystallite growth using the Ozawa and Kissinger methods respectively. A fitted value of $90.06\,\mathrm{kJ\,mol^{-1}}$ and $83.73\,\mathrm{kJ\,mol^{-1}}$ are obtained for the respective methods.

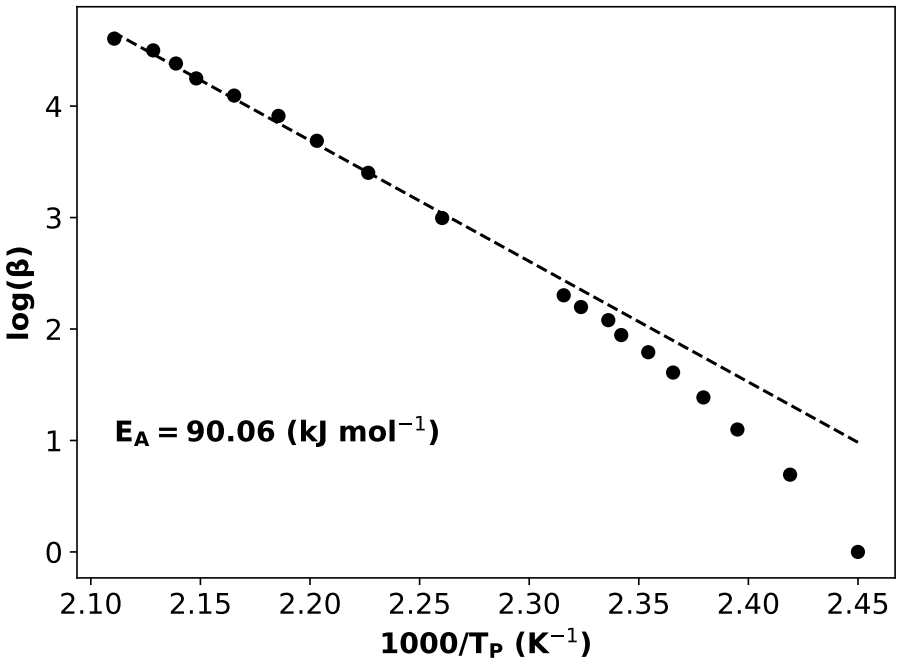

Figure S4: Ozawa plot used for extracting activation energy of crystallization.

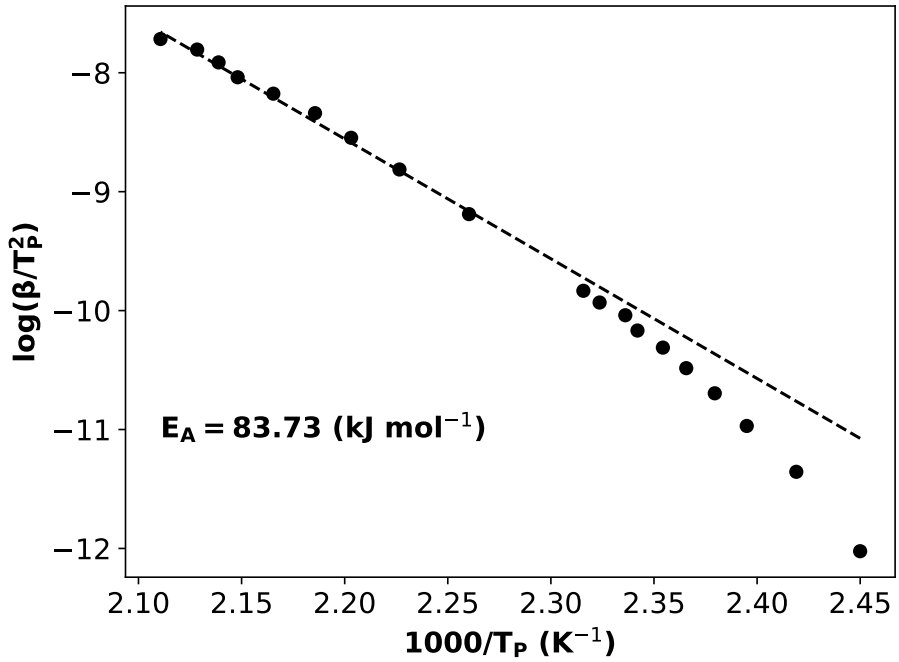

Figure S5: Kissinger plot used for extracting activation energy of crystallization.