Uncovering the Structural Characteristics of the Combinatorial Zinc Titanate Thin Film using Multimodal Modeling

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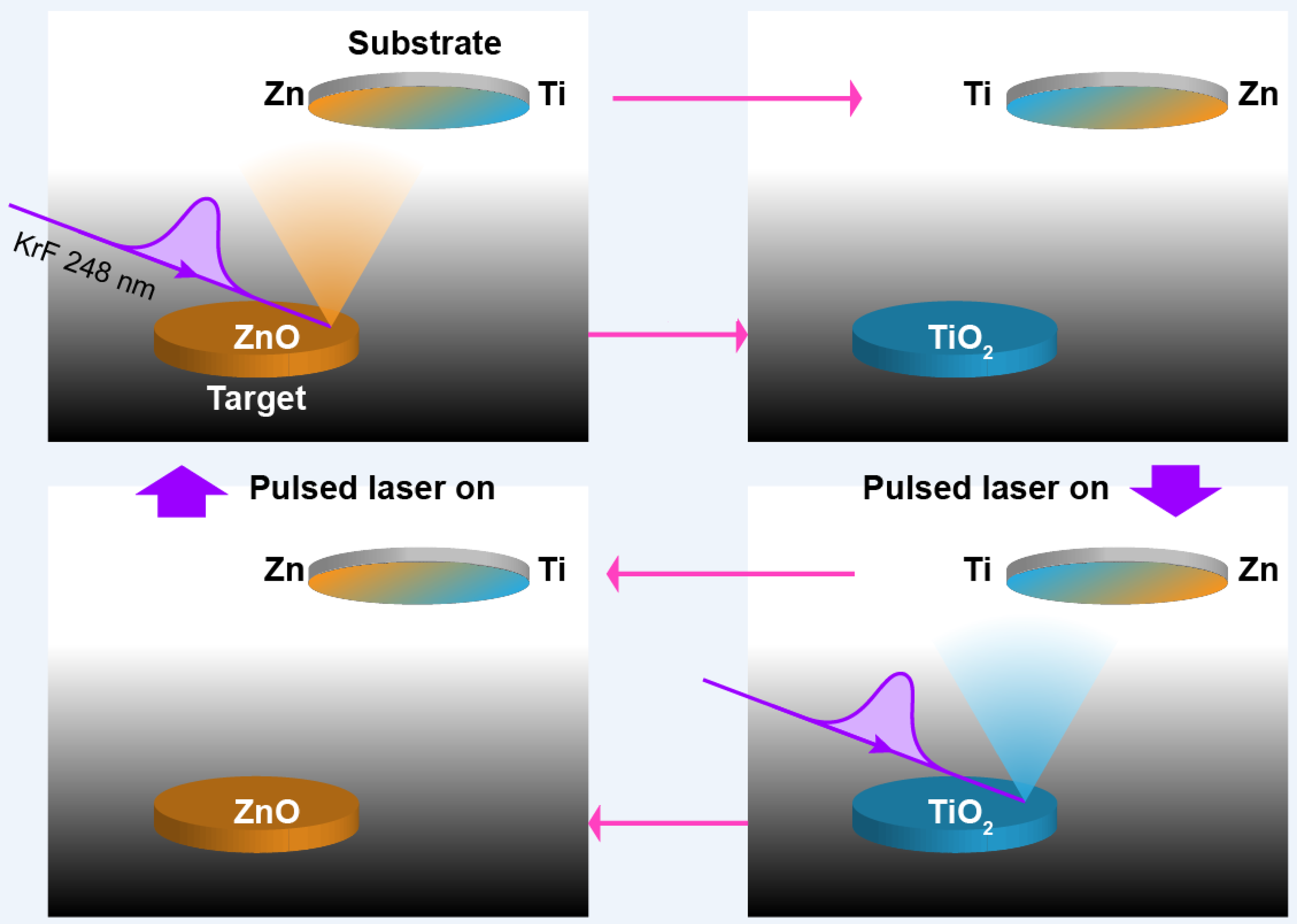
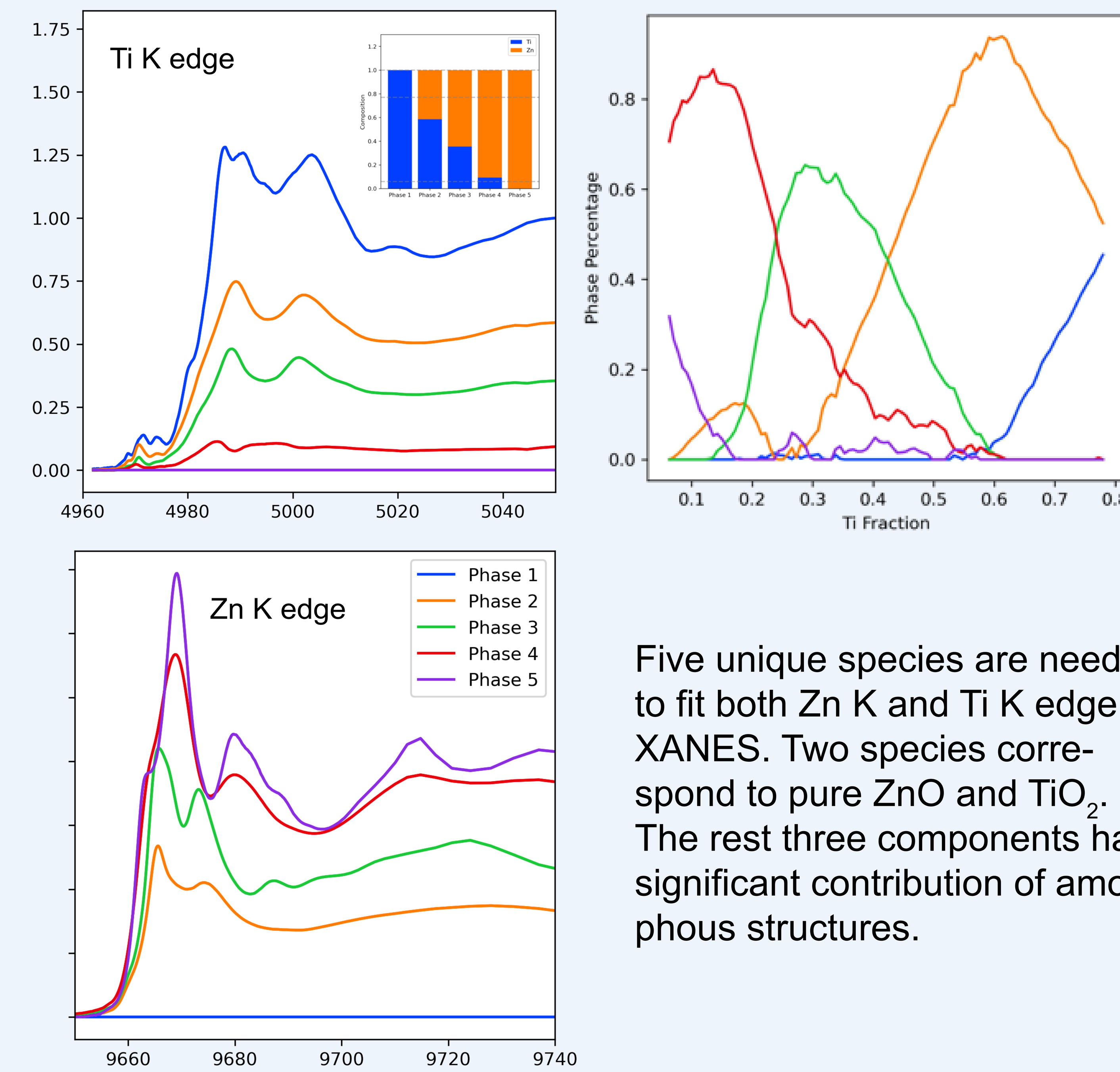
Zinc titanate is a metal oxide which has promising applications in microwave dielectrics, heterogeneous catalysis, photocatalysis, and energy storage due to its low cost, low toxicity, and good surface properties. However, the properties of the zinc titanate vary on the stoichiometry and different phases in the phase diagram. In order to understand how to control the growth of different phases of zinc titanate, a thin film is grown by combinatorial synthesis method with a monotonically increasing titanium zinc ratio. Multivariate curve resolution (MCR) analysis reveals five phases at different Ti concentration regions, including two known phases - ZnO and TiO_2. Three phases remain to be identified that has significant contribution of amorphous structures. We build defect structure models and construct simulated basis for Ti and Zn near edge X-ray absorption spectra. The spectral basis is used to fit the MCR spectral components. By analyzing regression weights on each basis, we identify three phases are comprised of different portion of low energy local motifs in $TiZn_2O_4$, $TiZnO_3$, $Ti_2Zn_3O_8$ compounds and defect structures. We further confirm the low Ti concentration phase as Ti defects in ZnO by analyzing the X-ray diffraction pattern and optical absorption spectra.

1. Thin film synthesis



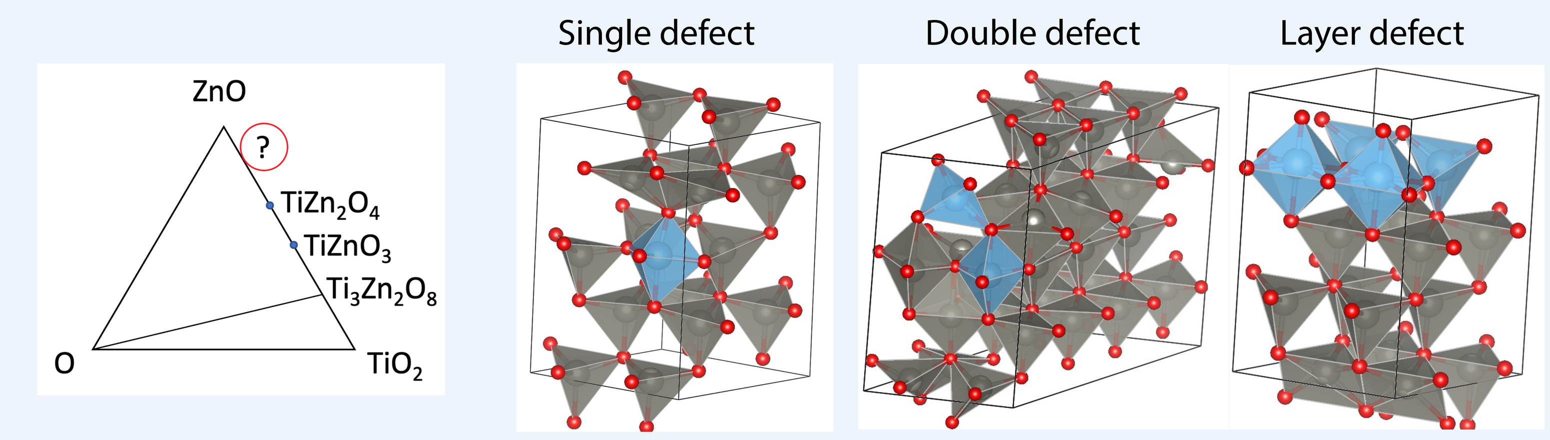
The thin film is grown by combinatorial synthesis method with a monotonically increasing titanium zinc ratio across the wafer surface.

2. Multivariate curve resolution (MCR) analysis



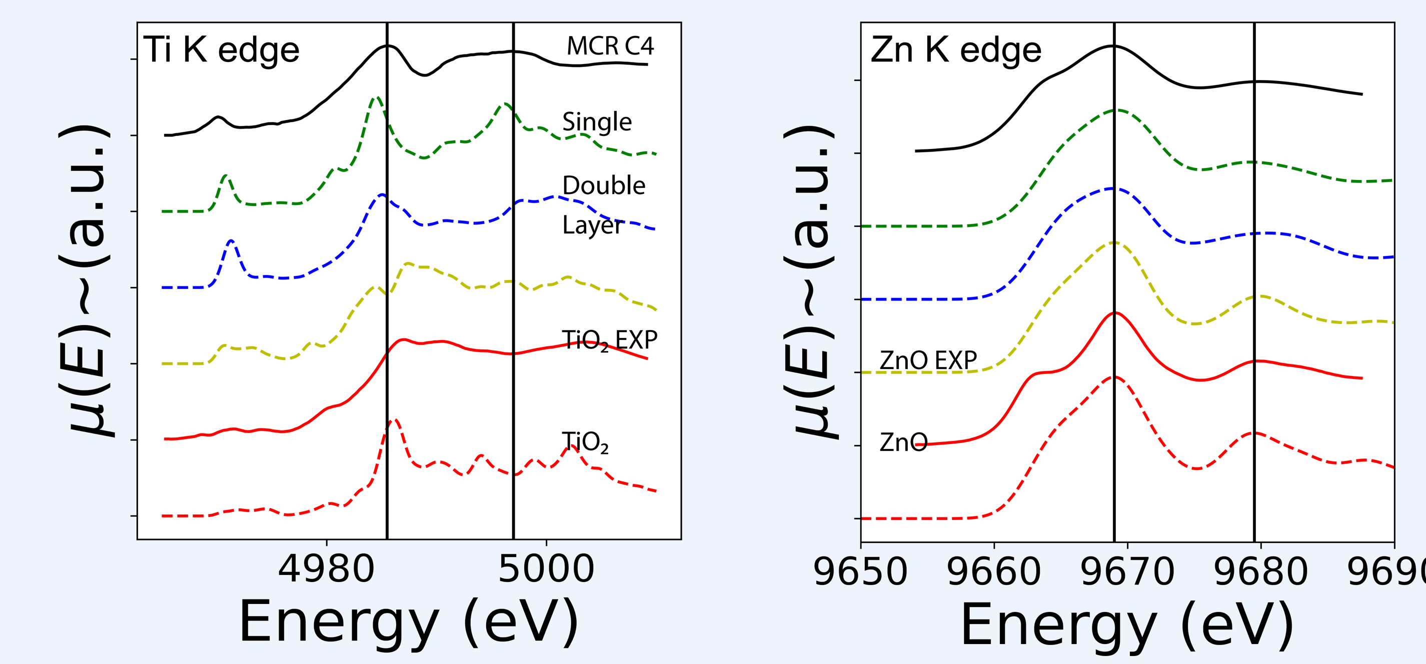
Five unique species are needed to fit both Zn K and Ti K edge XANES. Two species correspond to pure ZnO and TiO_2. The rest three components have significant contribution of amorphous structures.

3. Defect structures models



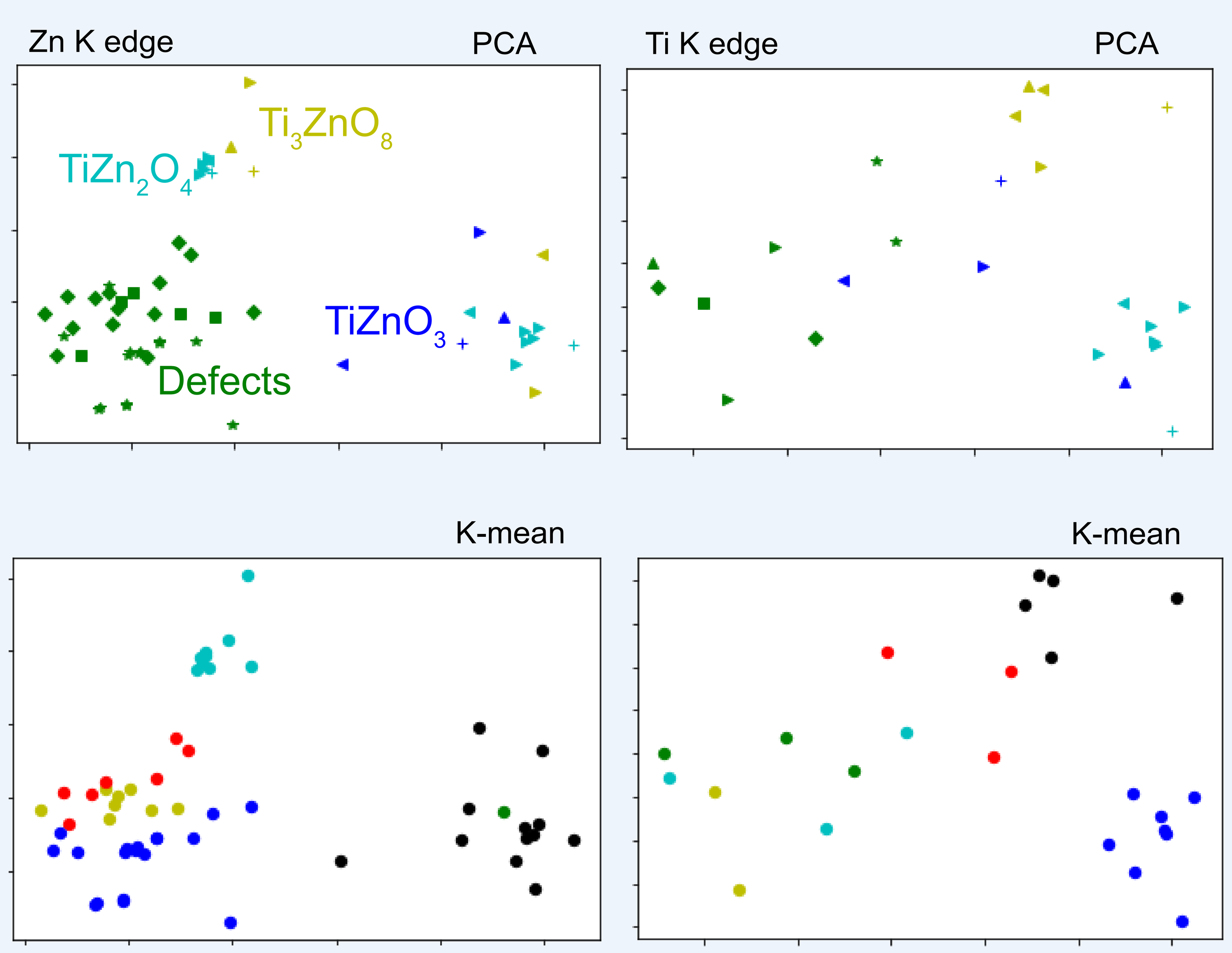
Formation energy/Ti: 2.48 eV | 1.87 eV | 0.97 eV

At low Ti concentration region, the Ti defects are metastable and tend to aggregate.



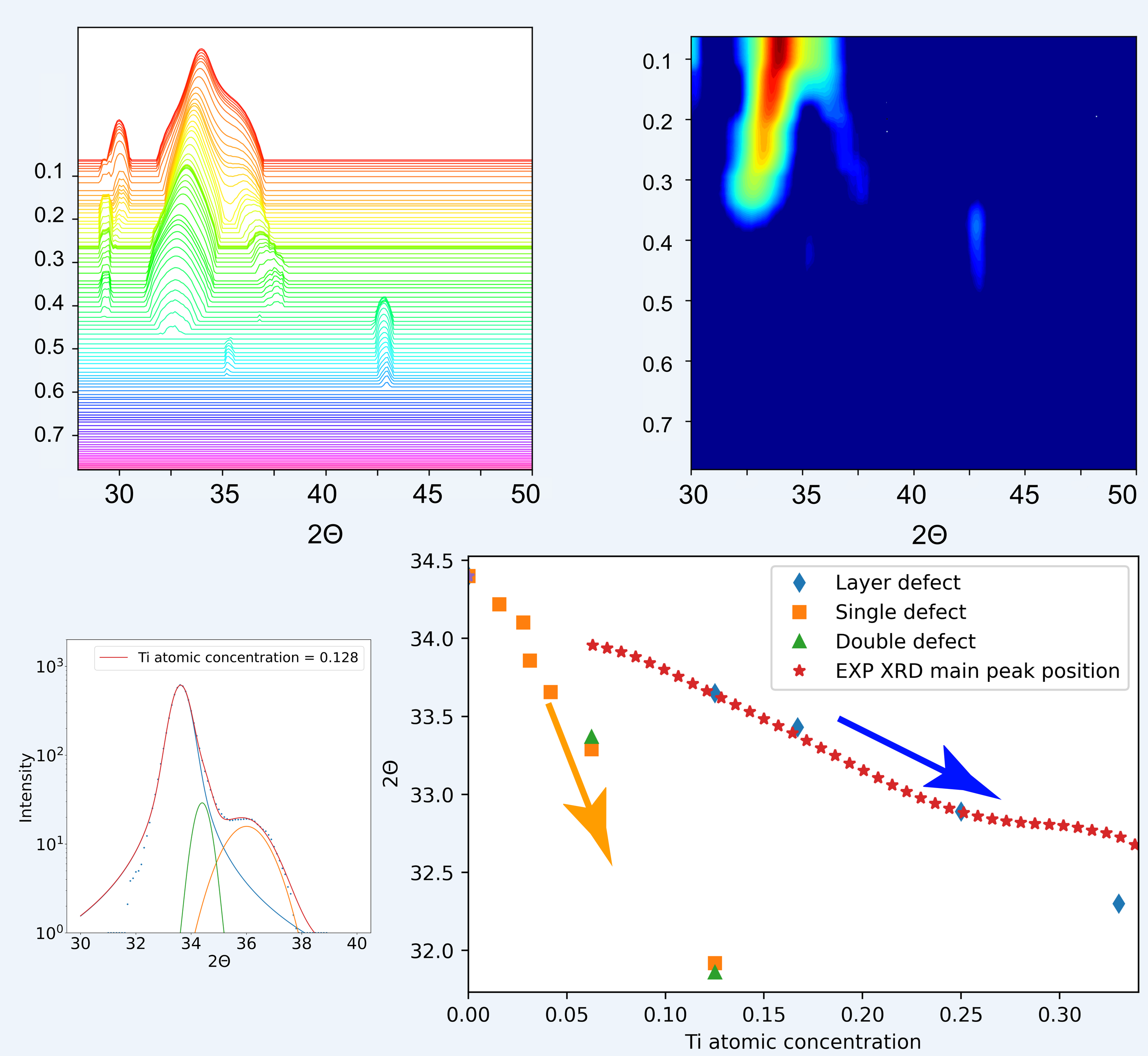
The MCR C4 spectrum can be decomposed into simulated XANES of defects.

4. Local motifs analysis



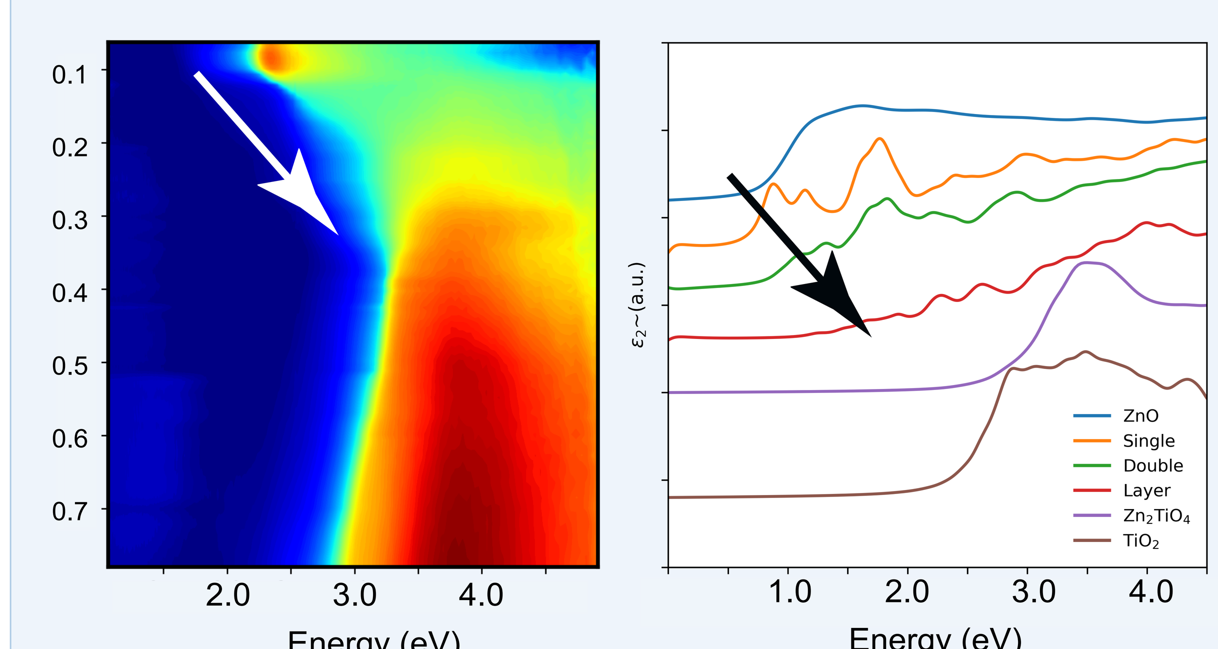
Linear regression fitting MCR spectra → MCR C2: Ti_3ZnO_8 $TiZnO_3$ Defects
MCR C3: $TiZn_2O_4$ Defects
MCR C4: Defects

5. Validate defect models by XRD



The layer defects can well fit the XRD peak shift trend.

6. Validate defect models by optical absorption spectra



Defect structure optical spectra simulations show optical gap increase compared to ZnO.

Conclusions

We report a combination of first principle method, total energy calculation, XANES simulation and optical spectra simulation to unveil the complex zinc titanate structure of the sample grown by combinitorial method. The proposed structure models are in good agreement with experimental mesurements

Acknowledgements

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