

Introduction

- In accordance with the Paris Climate Agreement, Australia will reduce its carbon emissions to 28% of their 2005 levels by 2050 [1].
- Australia is currently developing two technologies to assist in this transition: next-generation solid-oxide fuel cells and long-term storage for radioactive waste.
- Pyrochlores of the structure $A_2B_2O_7$ have been proposed as potential electrolytes in solid-oxide fuel cells due to their regularly repeating oxygen vacancies and structural stability [2]. Different types of disorder (in the form of chemical or structural defects) have been shown to improve the electrochemical properties of the material [3].
- We aim to investigate various properties of some pyrochlores to establish the feasibility of specifically engineering types of disorder to be used in next-generation application use.

Quantifying Order and Disorder

- We are focused on order and disorder at two length scales: long- and short-range.
 - Long-range average structure was investigated using synchrotron X-ray diffraction (S-XRD) and neutron powder diffraction (NPD), providing information on the symmetry of the cationic and anionic sublattices respectively.
 - Short-range local structure was investigated using X-ray absorption near-edge structure (XANES), providing information on the local geometry and coordination environments of the metal ions.

Synthesis Techniques

- A standard solid-state synthesis route was taken in preparing a series of $Tm_2(Ti_{2-x}Tm_x)O_{7-x/2}$ 'stuffed' pyrochlores. Tm_2O_3 and TiO_2 were preheated to 900 °C to remove adsorbed water and carbon dioxide.
- The solid-state solutions were annealed at 1000 °C and 1500 °C for 24 hours each, with grinding in between. The samples were slow-cooled at 0.1 °C min⁻¹ to ensure the crystallinity of the product.

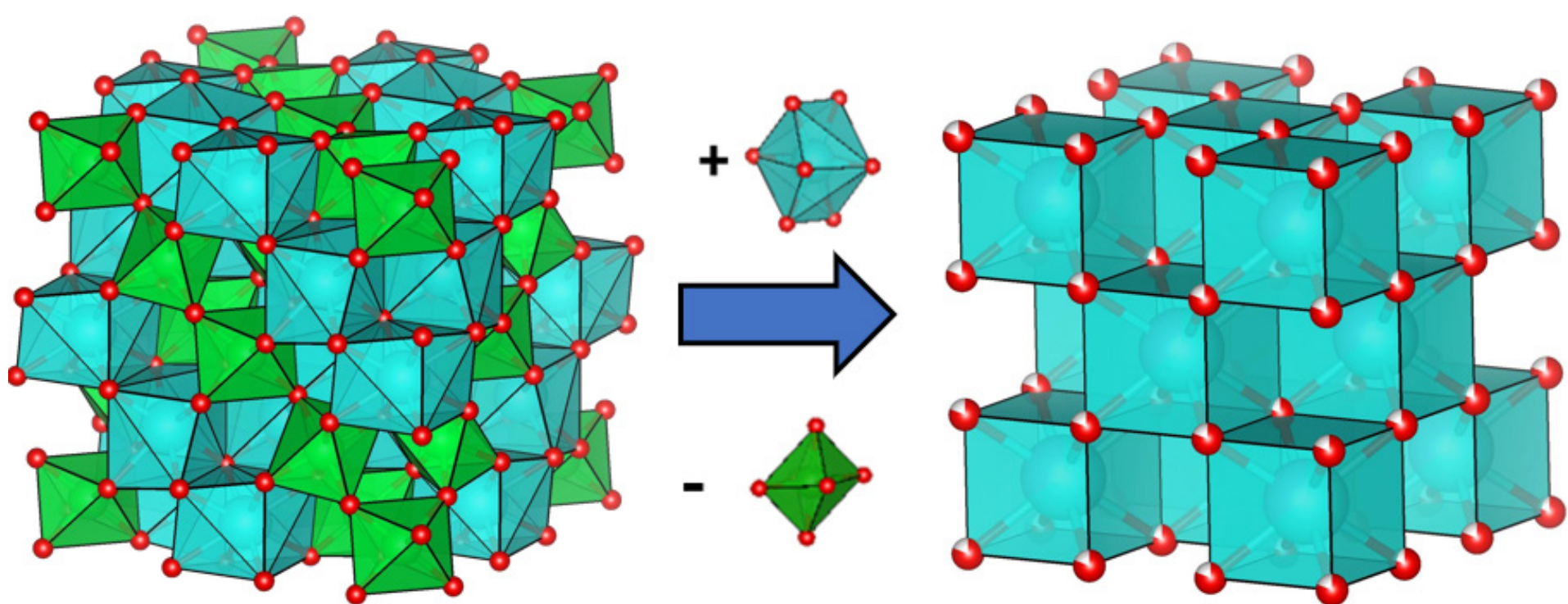


Figure 1: (Left) The ideal pyrochlore structure of $Tm_2Ti_2O_7$, showing thulium polyhedra (blue) and titanium octahedra (green). (Right) The defect-fluorite structure of Tm_2TiO_5 . A series of samples was constructed by gradually substituting more thulium onto the B-site of the structure.

Possible Applications – Oxygen-Ion Conductivity

- Ionic conductivity data was taken using Electrochemical Impedance Spectroscopy (EIS). An increase in conductivity is observed with a small amount of 'stuffing', and a sharp drop in conductivity afterwards.
- As Tm^{3+} is larger than Ti^{4+} , it is possible that the larger ions act as a bottleneck for anion diffusion. This is also seen in the distortion of the TiO_6 polyhedral and the formation of anti-site pairs [4].

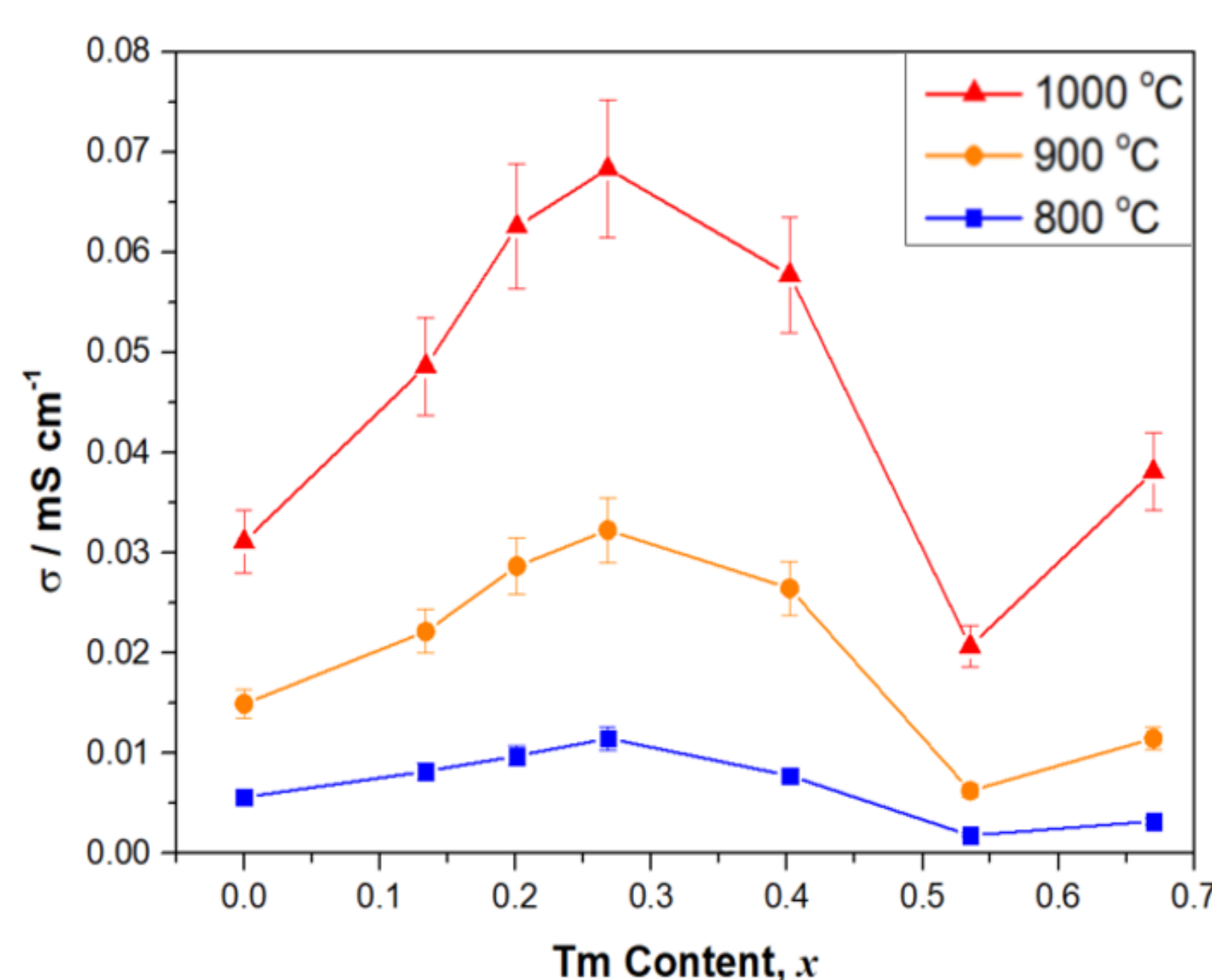


Figure 5: Temperature-dependent ionic conductivity for the $Tm_2(Ti_{2-x}Tm_x)O_{7-x/2}$ series, measured at operational temperatures comparable to solid-oxide fuel cells.

Conclusions

- S-XRD showed the $Tm_2(Ti_{2-x}Tm_x)O_{7-x/2}$ series to be either pyrochlore or a multiphase sample, as well as the evolution of anti-site pairs.
- NPD showed a persistent pyrochlore-like ordering of the oxygen anions, which was further supported by structure factor analysis.
- Short-range local structure shows a more gradual development of local disorder in the cation and anion sublattices. In particular, the CFS of the $Ti(3d)$ orbitals decreases reflecting the distortion of the titanium polyhedra.
- Small amounts of 'stuffing' increase ionic conductivity by over a factor of two, showing it is possible to tailor stuffed pyrochlores as potential electrolytes for solid-oxide fuel cells.

Long-Range Order – S-XRD Patterns

- Data were acquired at the Powder Diffraction beamline of the Australian Synchrotron at 17 keV.
- Patterns show the disappearance of superlattice reflections, as well as the segregation into a multiphase region from $x = 0.134$ and the onset of anti-site disorder pairs from $x = 0.402$.

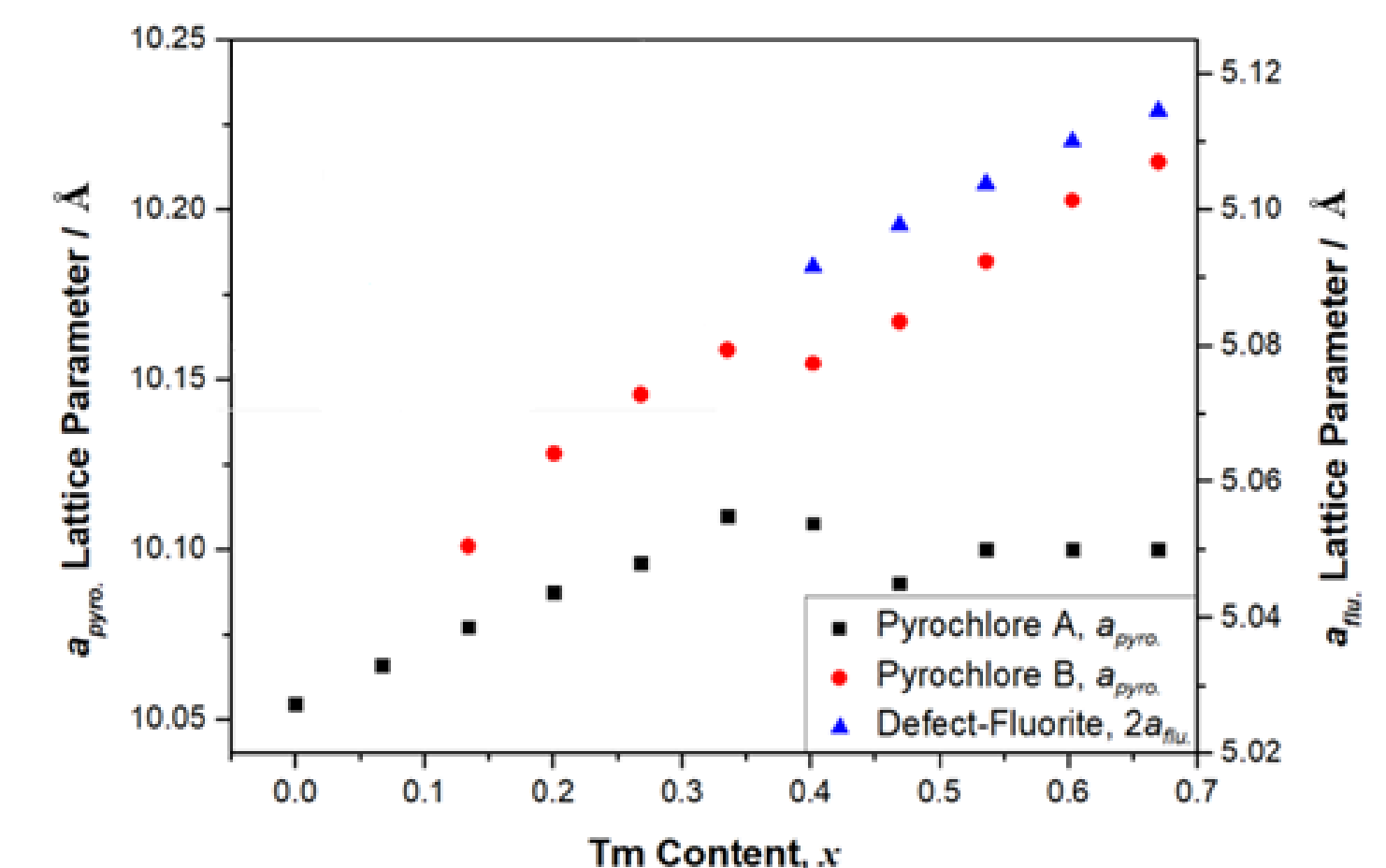
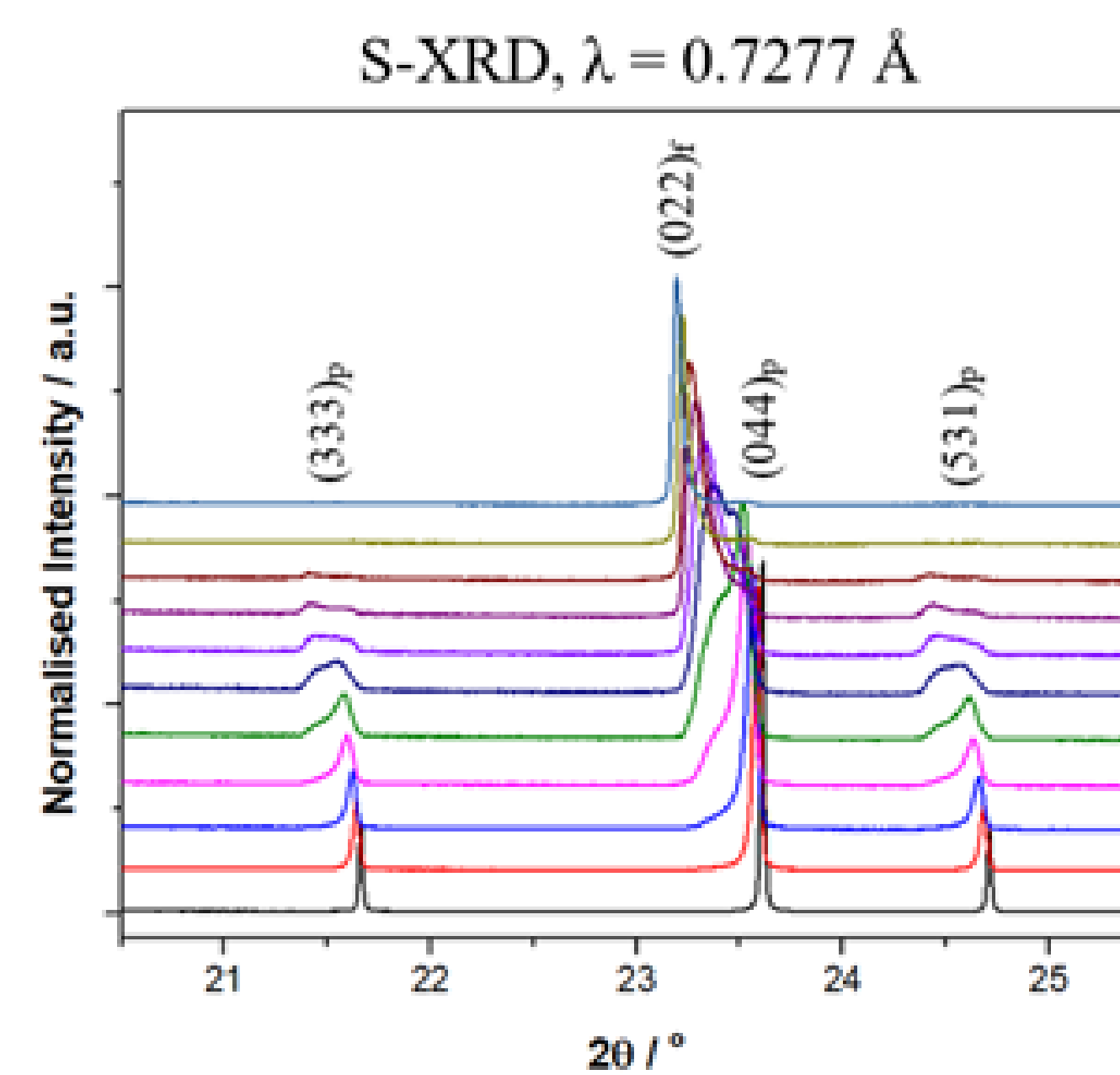


Figure 2: (Left) S-XRD patterns of the $Tm_2(Ti_{2-x}Tm_x)O_{7-x/2}$ series, showing the disappearance of superlattice reflections and multiphase regions. (Right) The lattice parameter of each phase.

Long-Range Order – NPD Patterns

- Data were acquired at the high-resolution powder diffractometer Echidna at the Open Pool Australian Lightwater (OPAL) reactor, operated by ANSTO. The wavelength of the incident neutrons were 1.6215 Å.
- Patterns show the persistence of certain superlattice reflections, demonstrating that pyrochlore-like ordering in the anions is present throughout the entire solid-solution series.
- Vacancies in the structure were localised to the O(48f) site.

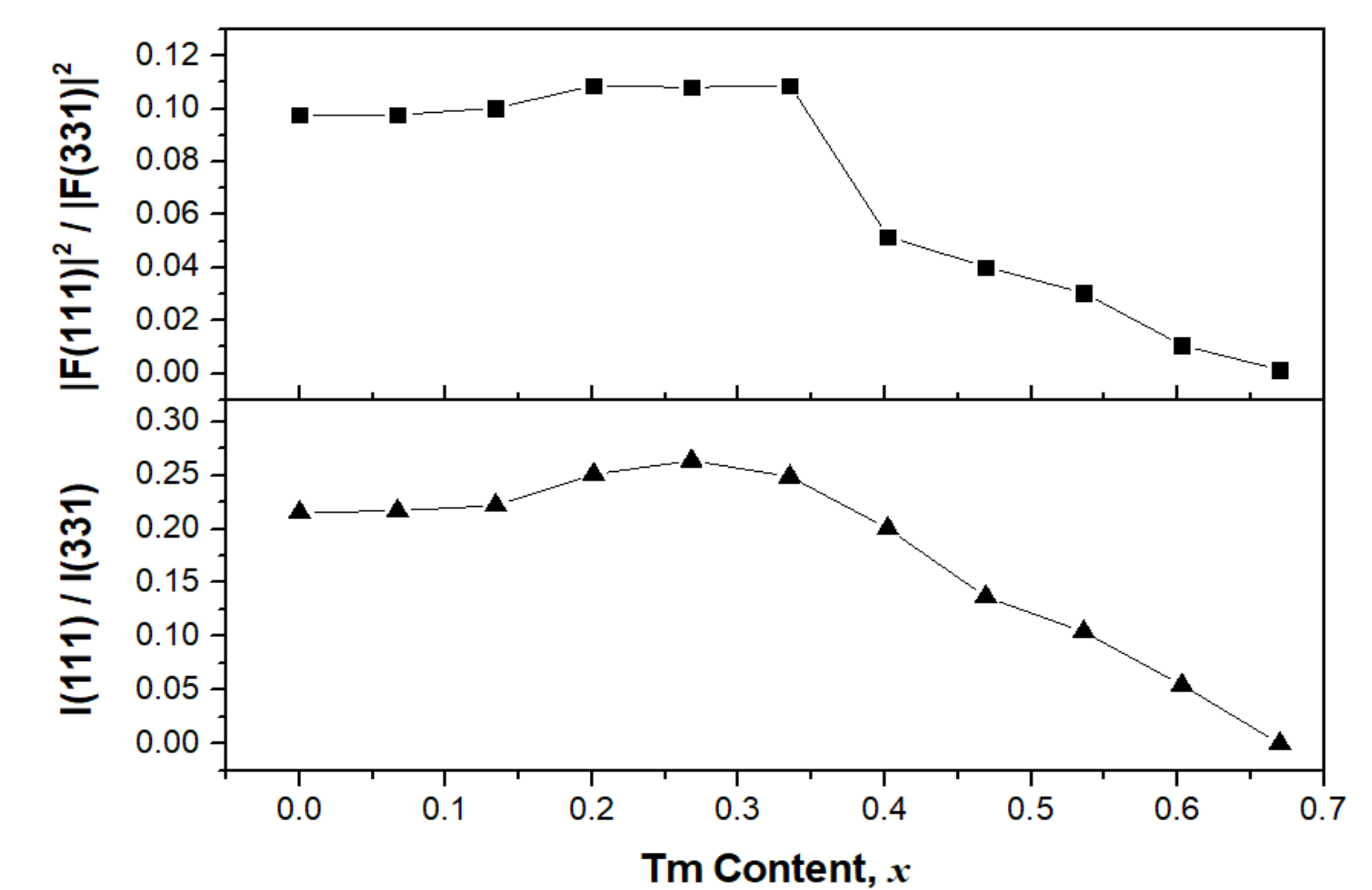
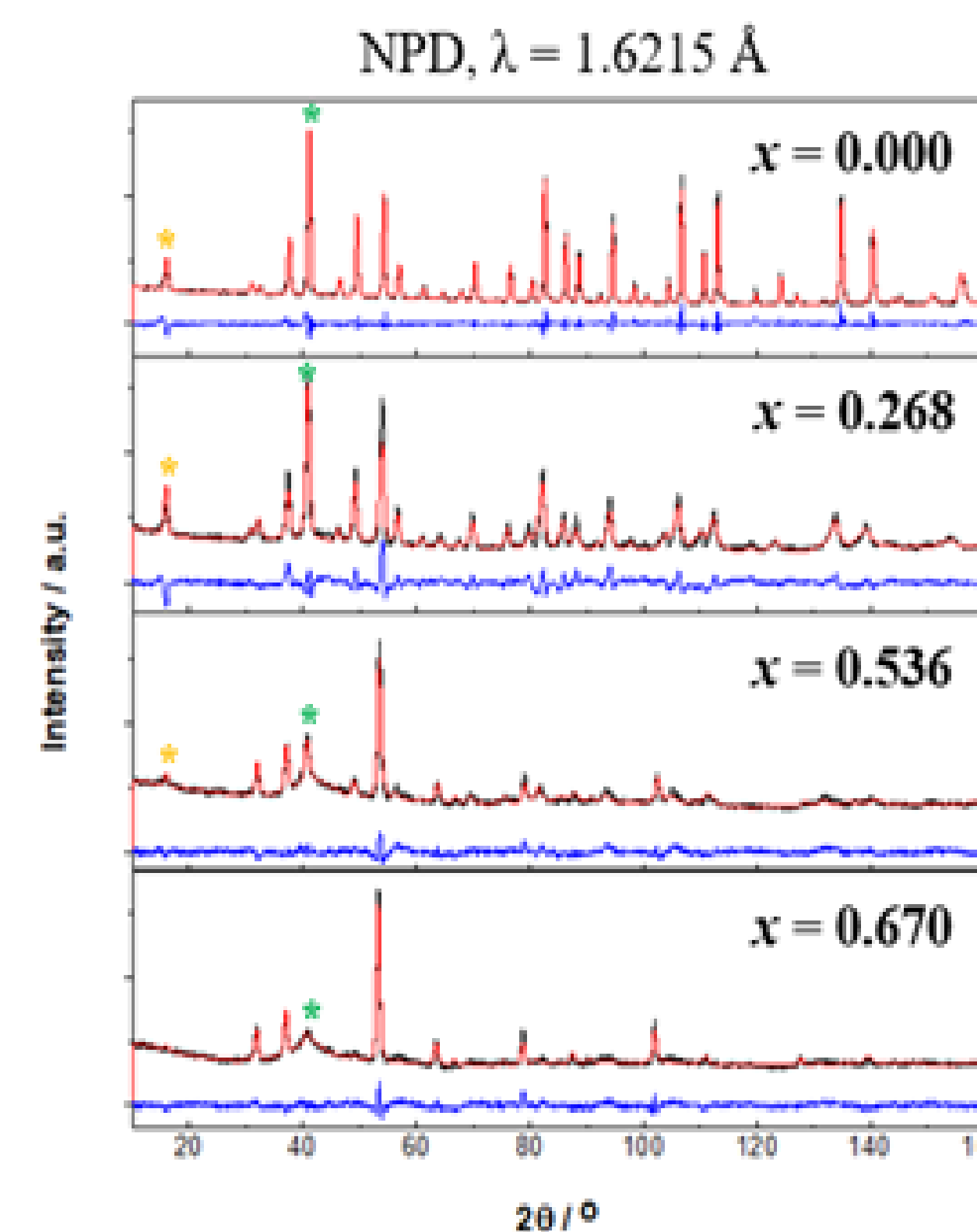


Figure 3: (Left) NPD patterns of the $Tm_2(Ti_{2-x}Tm_x)O_{7-x/2}$ series, with * denoting pyrochlore superlattice reflections. (Right) Comparing neutron structure factors for the $(111)_p$ and $(331)_p$ superlattice reflections, demonstrating pyrochlore-like anion ordering is present.

Short-Range Local Structure - XANES

- Data were acquired at the Soft X-Ray beamline of the Australian Synchrotron.
- The $Ti L_{3,2}$ -edge XANES spectra reveal information about the crystal field splitting (CFS), going from distorted octahedra to a seven-coordinated arrangement.
- A change in the line shape of Peak D is a medium-range effect observed in clusters of TiO_6 octahedra. The loss of resolved peak splitting can be explained by the decrease in CFS and an increase in medium-range disorder.

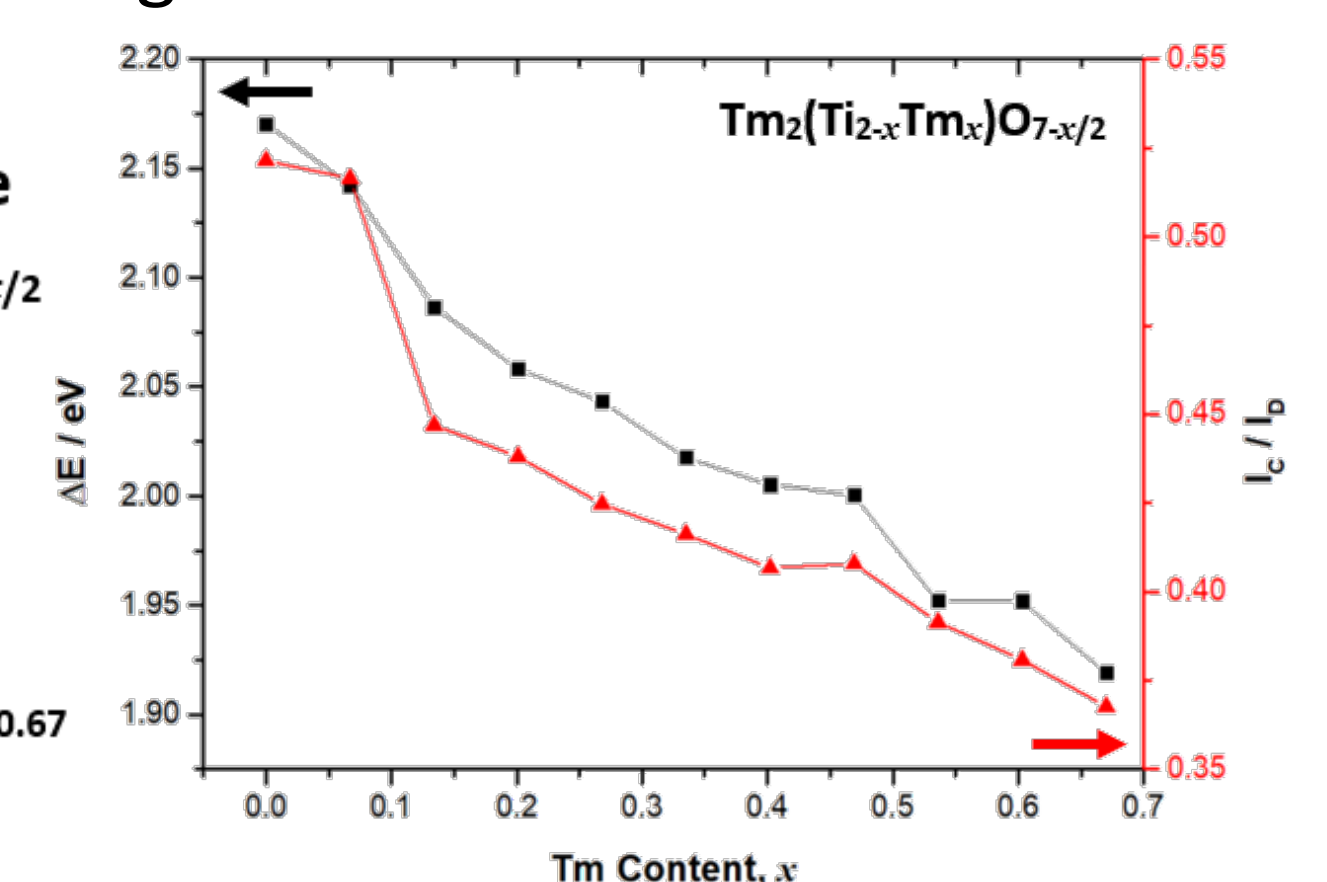
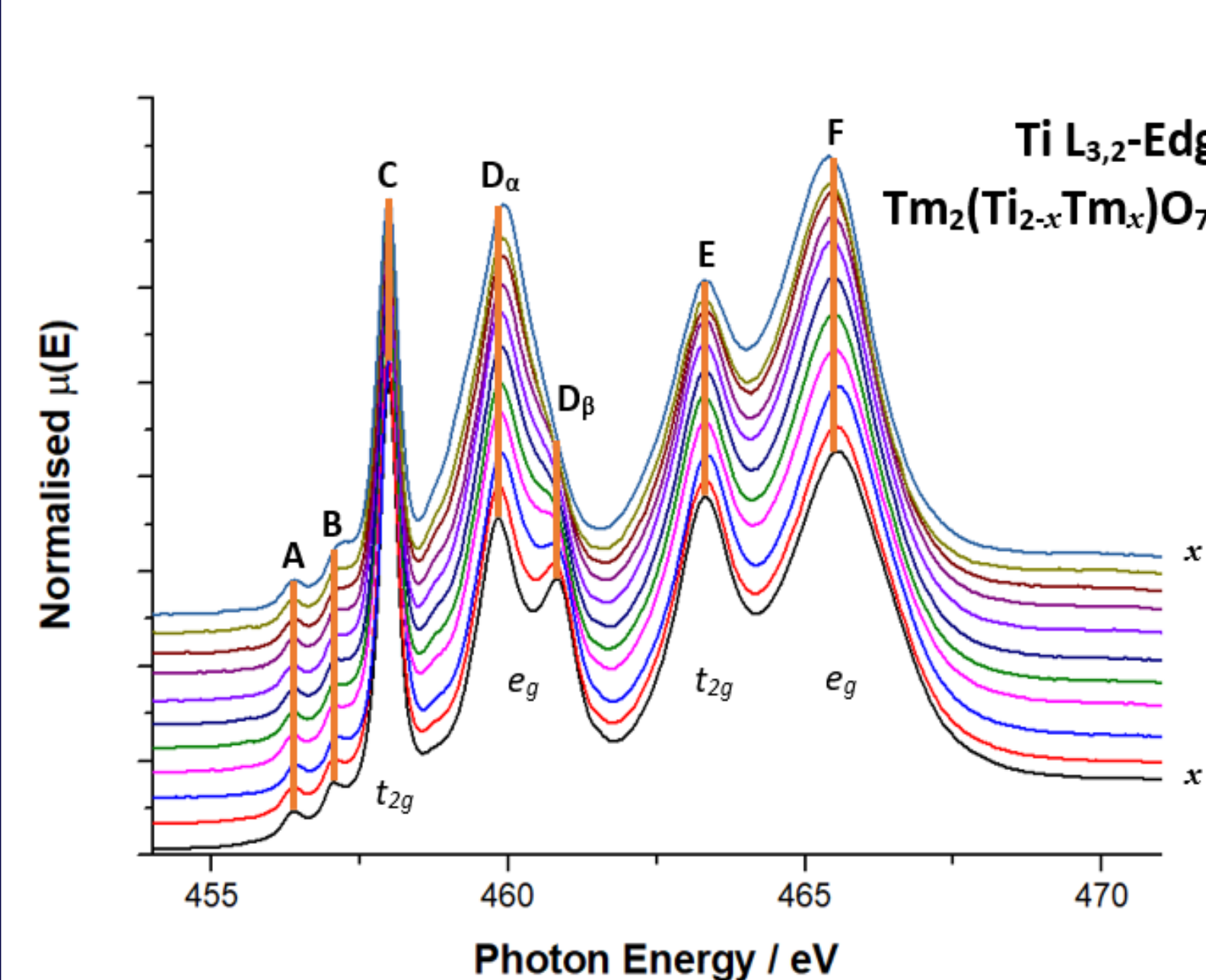


Figure 4: (Left) The $Ti L_{3,2}$ -edge of the $Tm_2(Ti_{2-x}Tm_x)O_{7-x/2}$ series. (Right) The crystal field splitting energy as a function of Tm^{3+} content (■) and the intensity ratio of Peaks C and D in the sample series (▲).

References

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- [2] Moon, P. K. et al.; *Solid State Ionics*, **1988**, 28-30 (1), 470-474.
- [3] Diaz-Guillen, J. A.; et al.; *J. Cond. Mat. Phys.*, **2007**, 19 (35), 356212.
- [4] Mullens, B. G. et al.; *In Preparation*.