Substitutional Doping of Transition Metal Antimonates

and the insights gained through neutron diffraction on ECHIDNA

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INTRODUCTION

Most compounds of formula MSb_2O_6 are based on the rutile structure (like TiO_2 and SnO_2)

- Trirutile forms through a tripled *c* axis through the M-Sb-Sb-M… bonds
- Network of corner and edge sharing octahedra
- $NiSb_2O_6$, $ZnSb_2O_6$, $CoSb_2O_6$ and other similar transition metal oxides exist in a tetragonal phase (s.g. *P*4_2*/mnm)*
- $CuSb_2O_6$ has an monoclinic distortion due to Jahn Teller effects dominating the structure (s.g. *P*2_1*/n*) [1]
- $CuSb_2O_6$ undergoes a second order phase transition to the tetragonal phase between 100°C – 150°C [2]

PHASE CHANGES

This monoclinic crystal structure cannot become tetragonal without an orthorhombic intermediate.[3]

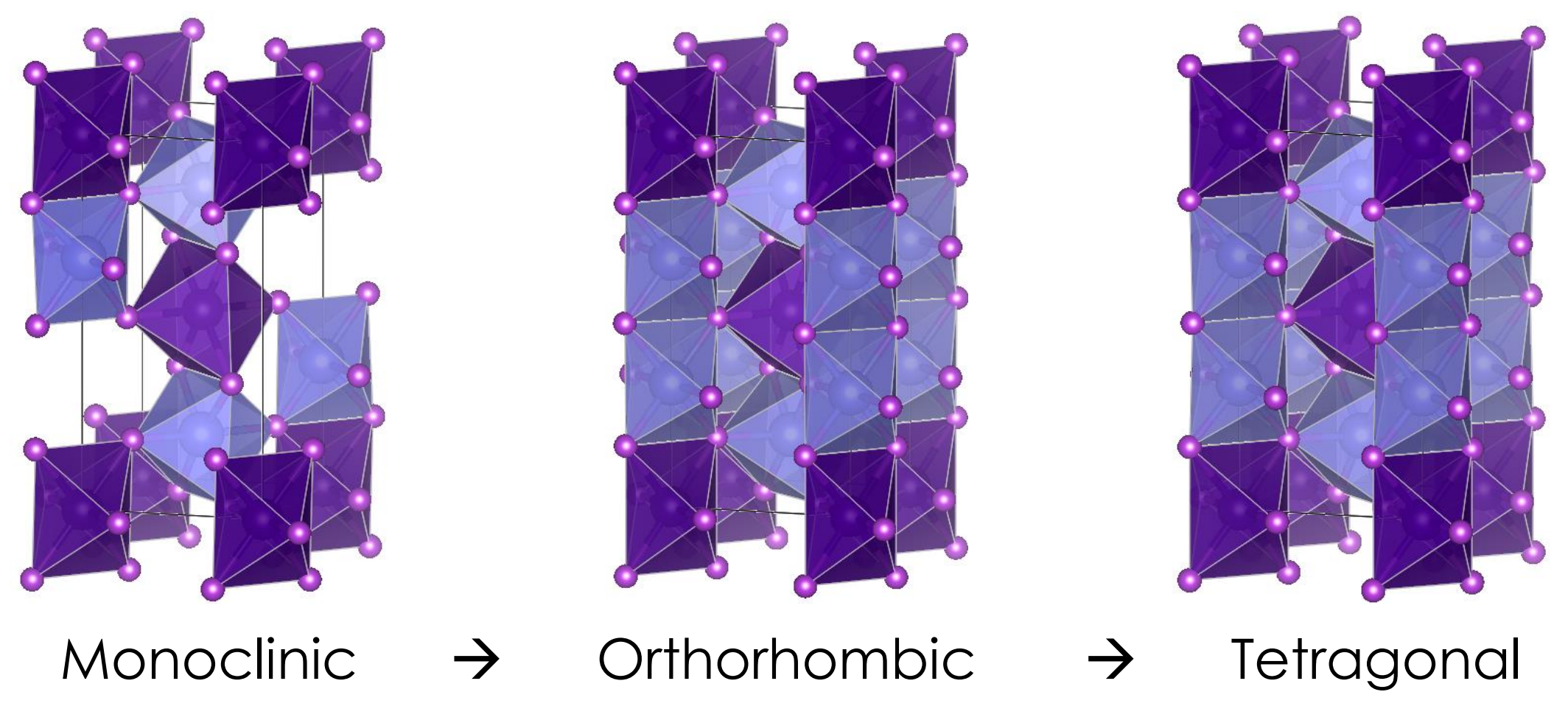

Figure 1: Monoclinic to Tetragonal phase transition through Orthorhombic intermediate

APPLICATIONS

Metal antimonates already make for interesting materials. Doping the structure allows for fine tuning of their properties to make them suitable for a variety of applications.

- Doping atoms with a similar size but different oxidation state reduces the oxygen occupancy in the structure.
- Oxygen vacancies create channels for oxygen ions to conduct. This is of research interest in use as solid oxide fuel cells and oxygen separation membranes
- The materials can also have interesting magnetic properties depending on what sits on the metal position or on the antimony position.

$Cu_{1-x}Ni_xSb_2O_6$

The phase transition of $CuSb_2O_6$ is of interest to us as the orthorhombic intermediate has never been reported. The primary aim of this project was to investigate the phase change behaviour of the compound, and whether this could be altered or controlled through Ni doping. HTNPD was used to investigate oxygen occupancy in the material.

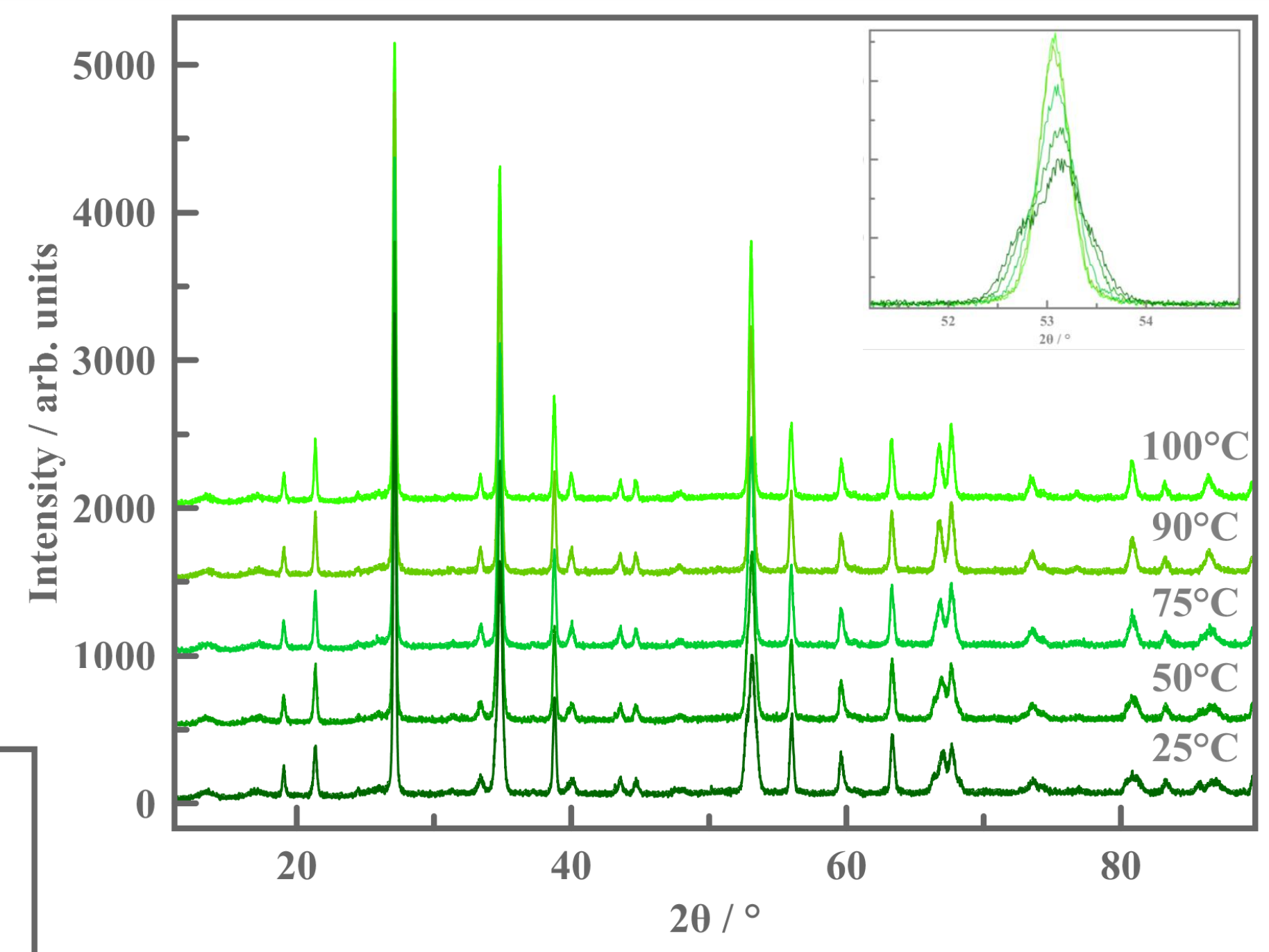

Figure 2: HT lab XRD patterns of $Cu_{0.8}Ni_{0.2}Sb_2O_6$

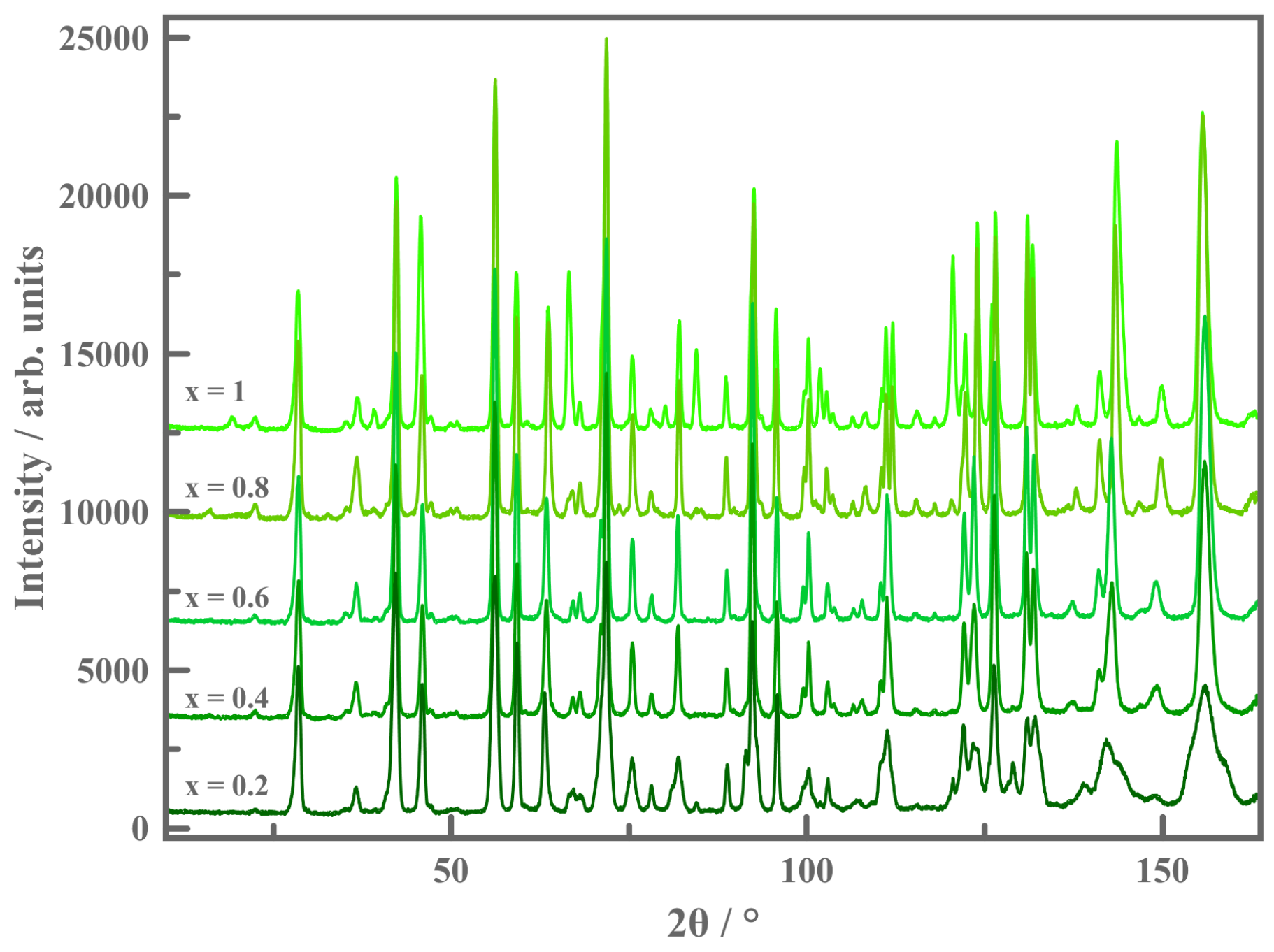

Figure 3: NPD patterns of $Cu_{1-x}Ni_xSb_2O_6$ collected at RT

- Where x > 0.4, a sole tetragonal phase formed
- Where x < 0.4, a mixed monoclinic and tetragonal phase was present
- Through XAS, it was found that some Cu^{2+} was reduced to Cu^{1+}
- Cu^{1+} increased with increased doping
- Oxygen deficiency increases with increased doping

$CoSb_{2-x}Ta_xO_6$

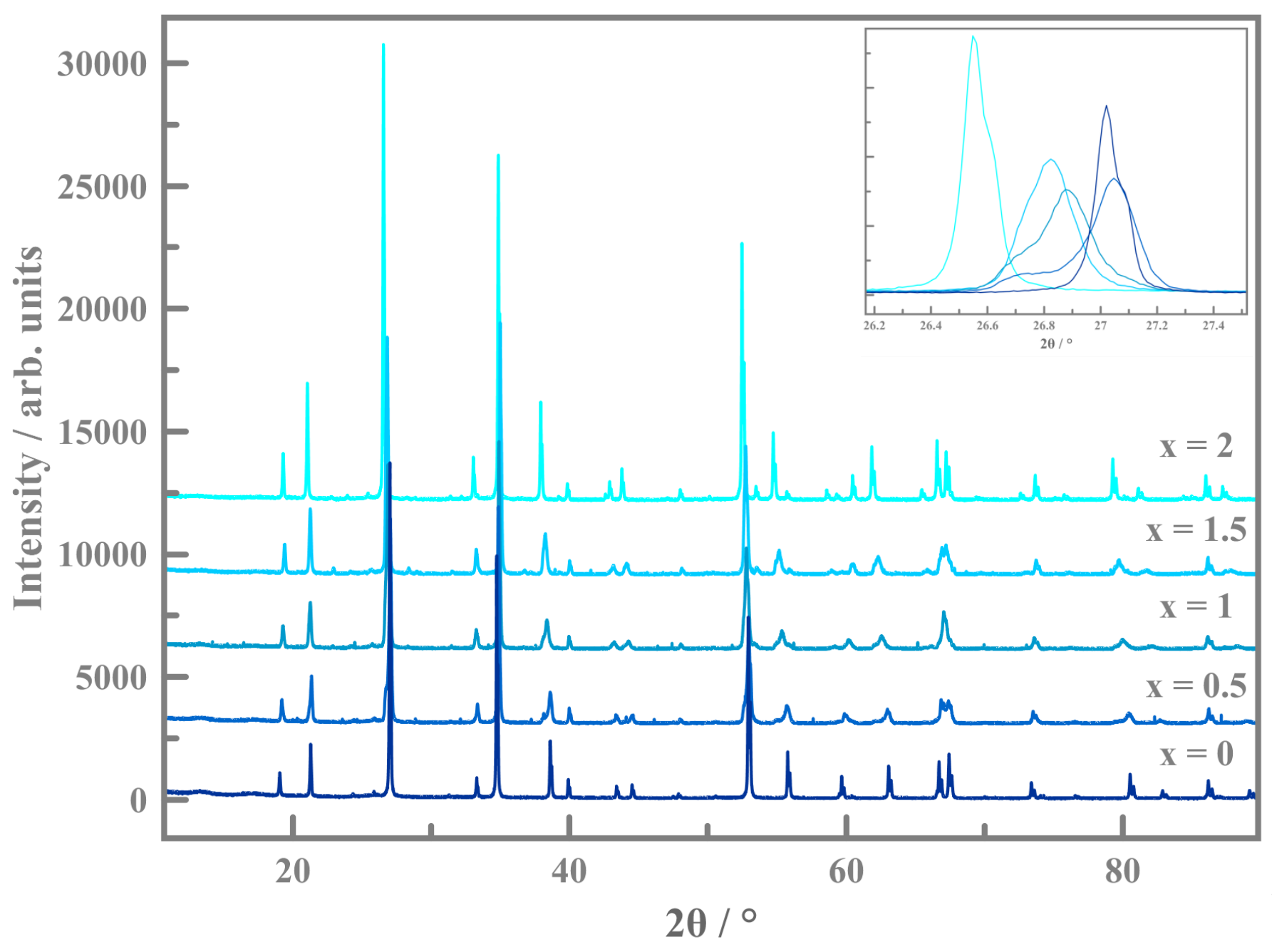

Figure 4: XRD patterns of $CoSb_{2-x}Ta_xO_6$

$CoSb_2O_6$ hosts antiferromagnetic ordering whilst isoelectronic $CoTa_2O_6$ hosts helical AFM ordering. [5] The primary aim of this project is to investigate the evolution of the ordering into a helical ordering with doping. Low temperature neutron experiments were carried out on these samples last week with data analysis still underway.

- Standard synthesis at 1050°C for 48 hours only produced phase pure product for x = 0, 2
- $CoSb_{0.5}Ta_{1.5}O_6$ could be made phase pure by synthesis under vacuum at 1050°C for 48 hours
- Work on synthesis of other compositions still undergoing
- Evident difference in NPD pattern for x = 2 and x = 1.5 at 4K.

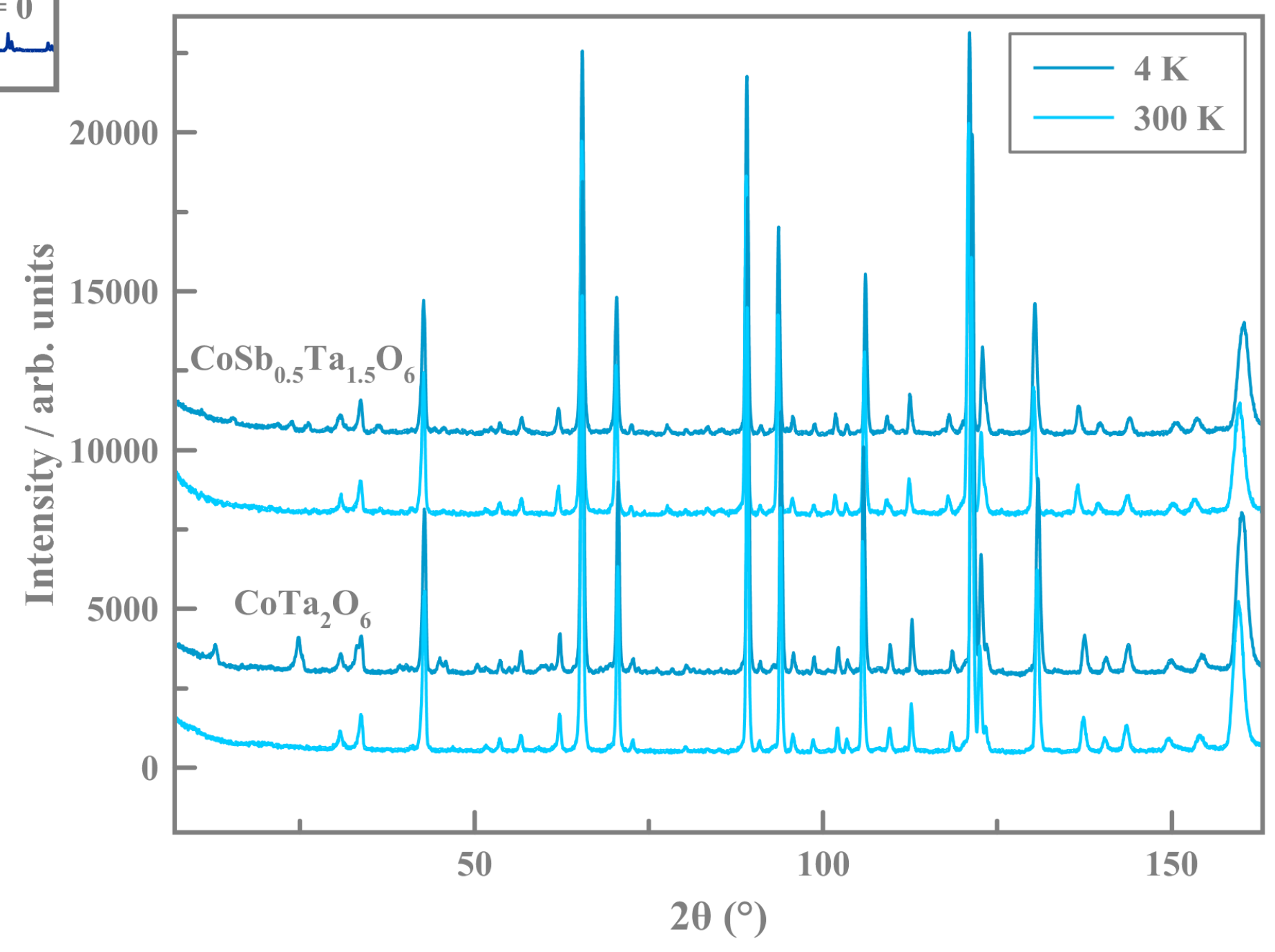

Figure 5: NPD patterns of $CoSb_2O_6$ and $CoSb_{0.5}Ta_{1.5}O_6$ at 4K and RT

$ZnSb_{2-x}Sn_xO_{6-x/2}$

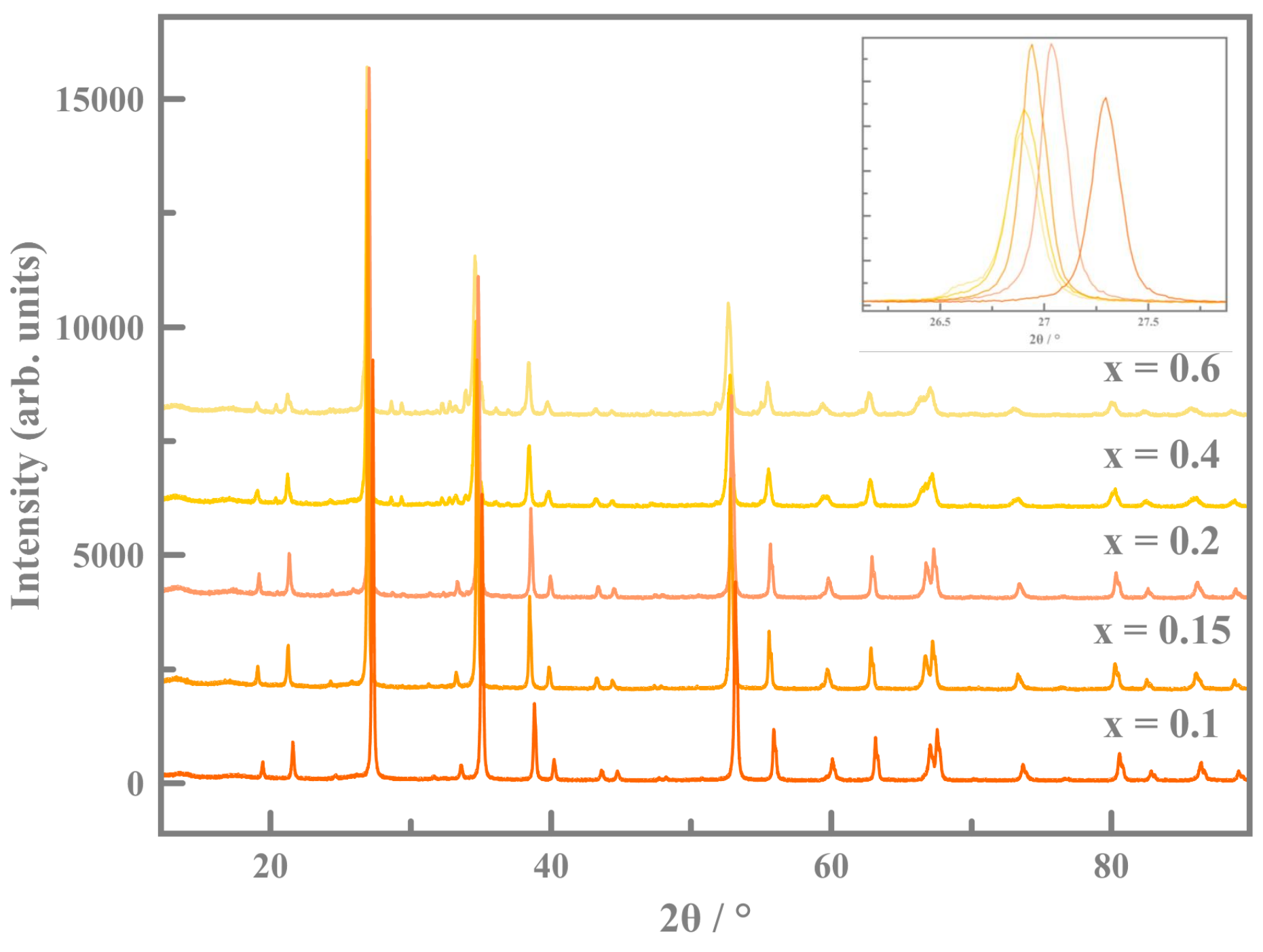

Figure 6: Lab XRD of $ZnSb_{2-x}Sn_xO_6$

$ZnSb_2O_6$ has recently garnered attention as a possible transparent conducting oxide. The primary aim of this project is to investigate how Sn doping changes the structure and properties of $ZnSb_2O_6$. HTNPD was initially used to investigate oxygen occupancy in the material, but the similar coherent scattering lengths of Zn, Sb and Sn created issues in differentiating these atoms through NPD.

- x = 0, 0.1 made phase pure by synthesis in air at 1100°C for 48 hours
- Compositions with increased doping could not be made phase pure as SnO_2 impurities were left over
- Despite the SnO_2 impurities, doping can be confirmed successful through observed increase in unit cell size
- Neutron diffraction indicates a net oxygen deficiency in x = 0.1
- Band gap decreases with doping

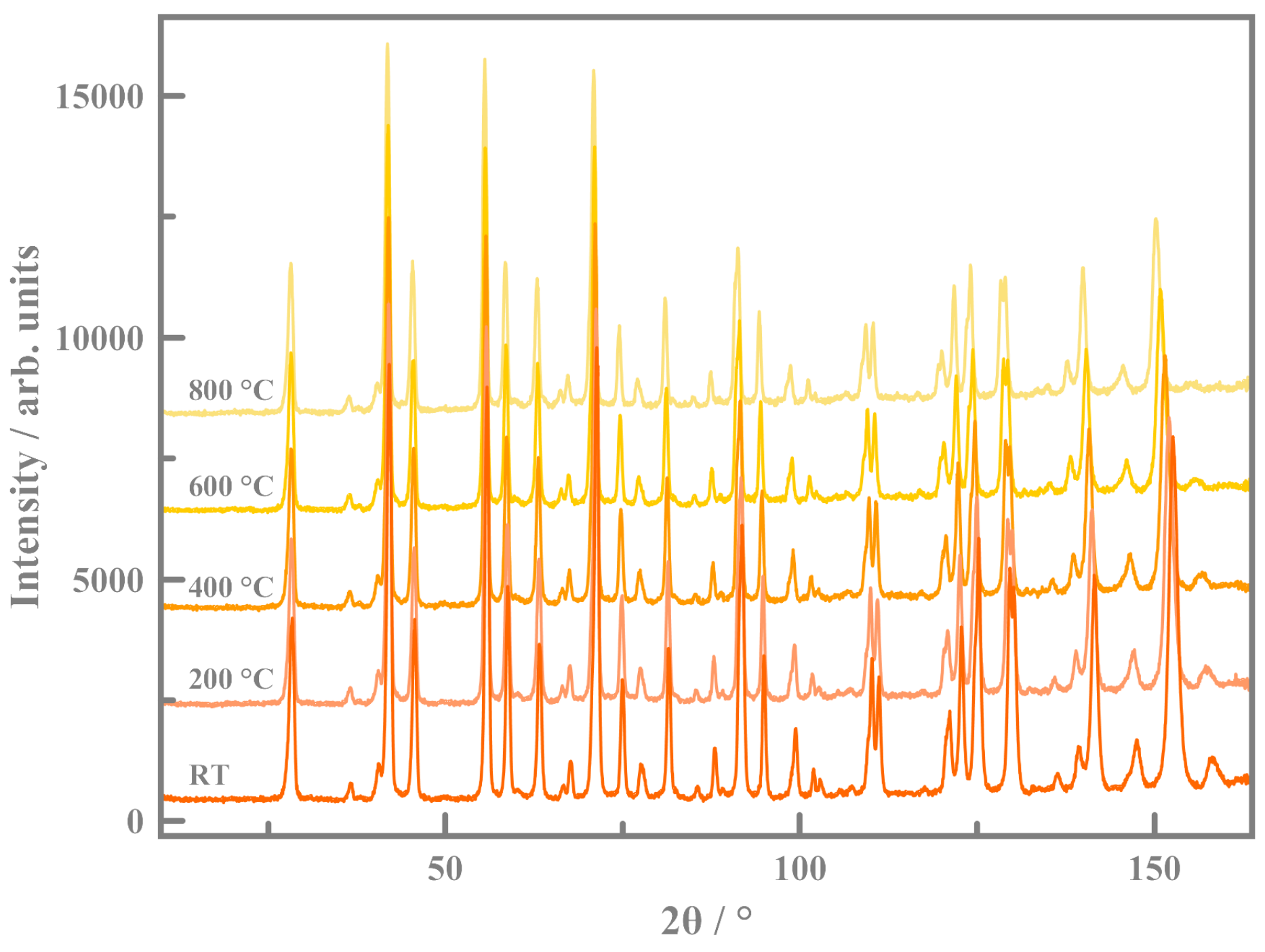

Figure 7: HTNPD $ZnSb_{2-x}Sn_xO_6$

$NiSb_{2-x}Sn_xO_{6-x/2}$

This series is one of the most recent to be added to this project to see how Sn doping could affect the $NiSb_2O_6$ structure. It was hypothesised that oxygen vacancies would be created like $ZnSb_{2-x}Sn_xO_6$, and this was investigated through NPD.

$CuSb_{2-x}Sn_xO_6$ was also of research interest but synthesis attempts on this material failed.

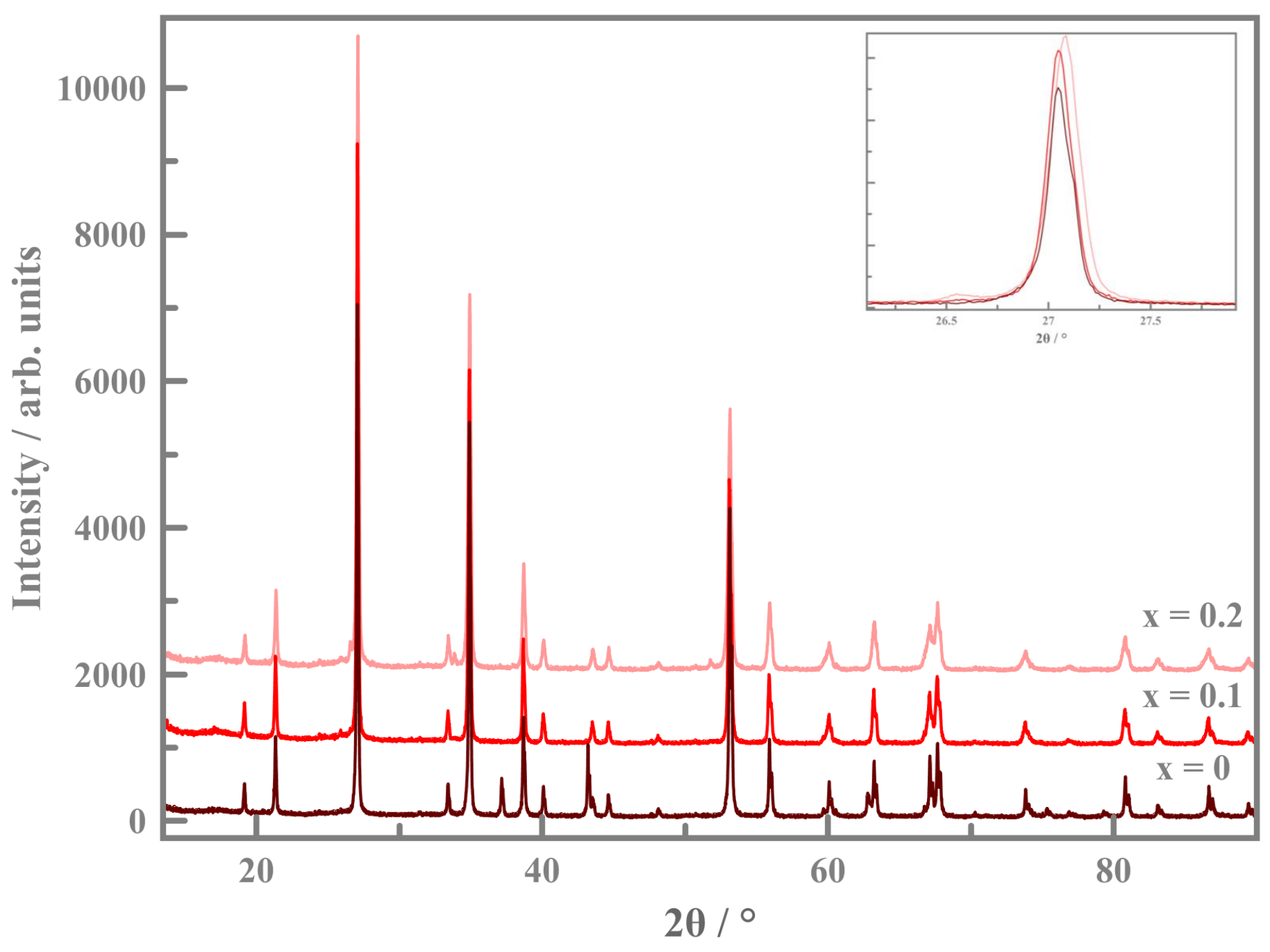

Figure 8: Lab XRD of $NiSb_{2-x}Sn_xO_6$

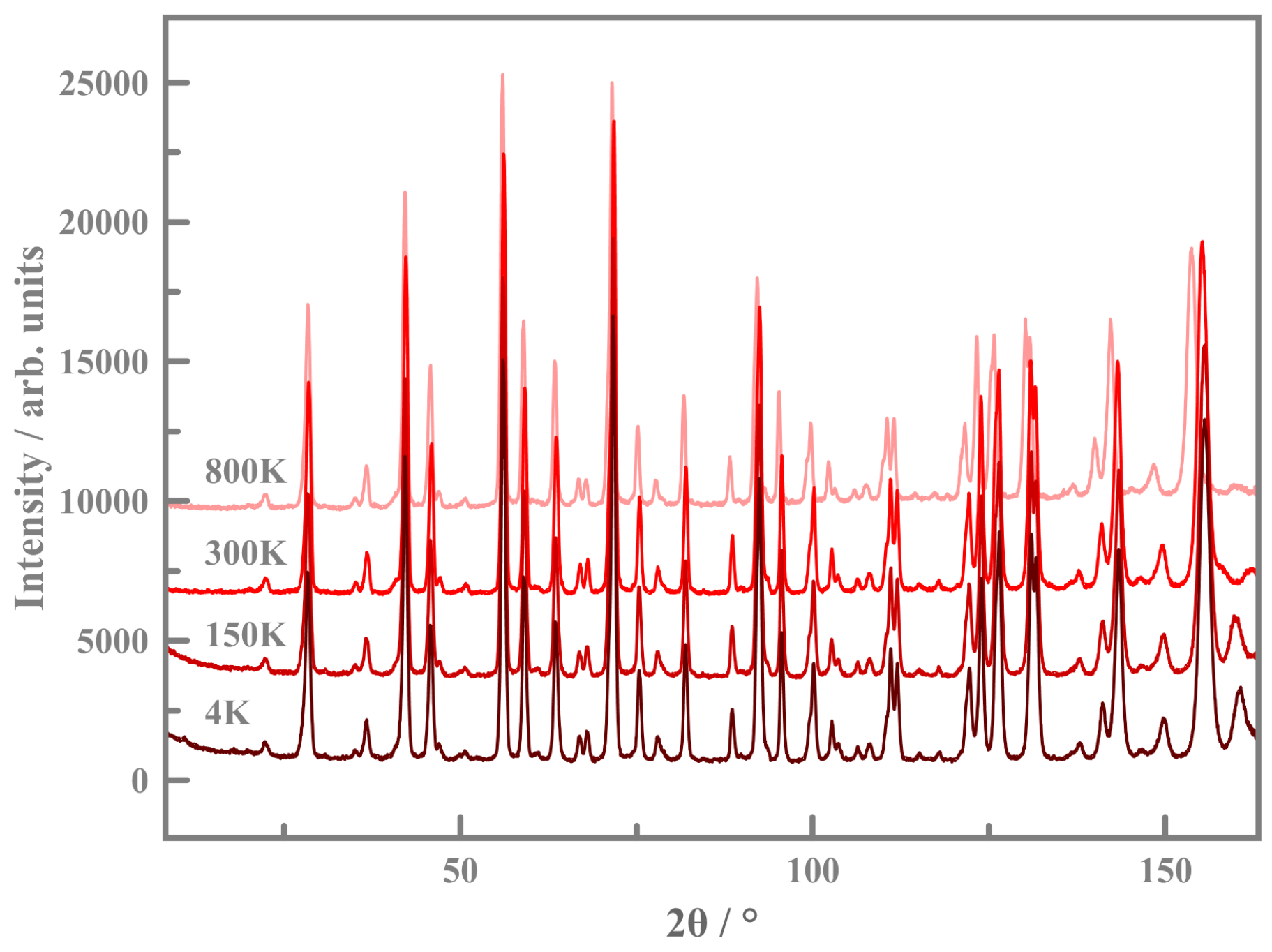

Figure 9: High and low temperature NPD of $NiSb_{2-x}Sn_xO_6$

- NiO impurities remained present in most samples, required >50% excess Sb_2O_3 as Sb is often lost to the vapor phase
- A net oxygen deficiency was observed where x = 0.1
- NPD also indictated a possible mixed occupation of Ni on the Sb/Sn position (4f)

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This poster draws information from the following:

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