Synthesis and Characterization of $CeNbO_{4+\delta}$ for Gas Permeation Membranes and SOFC Applications

Fride Vullum

Acknowledgments:

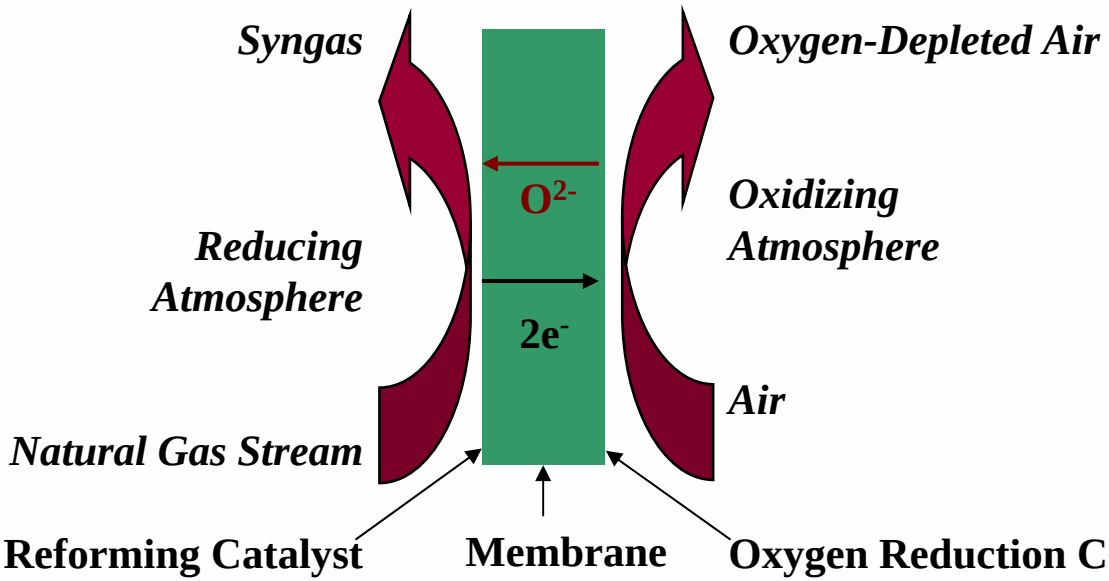
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Introduction

- Development of thin films for fuel cells and gas permeable membranes using proton and oxygen conducting materials.
- $CeNbO_4$ is a potential material for SOFC electrodes as well as gas separation membranes



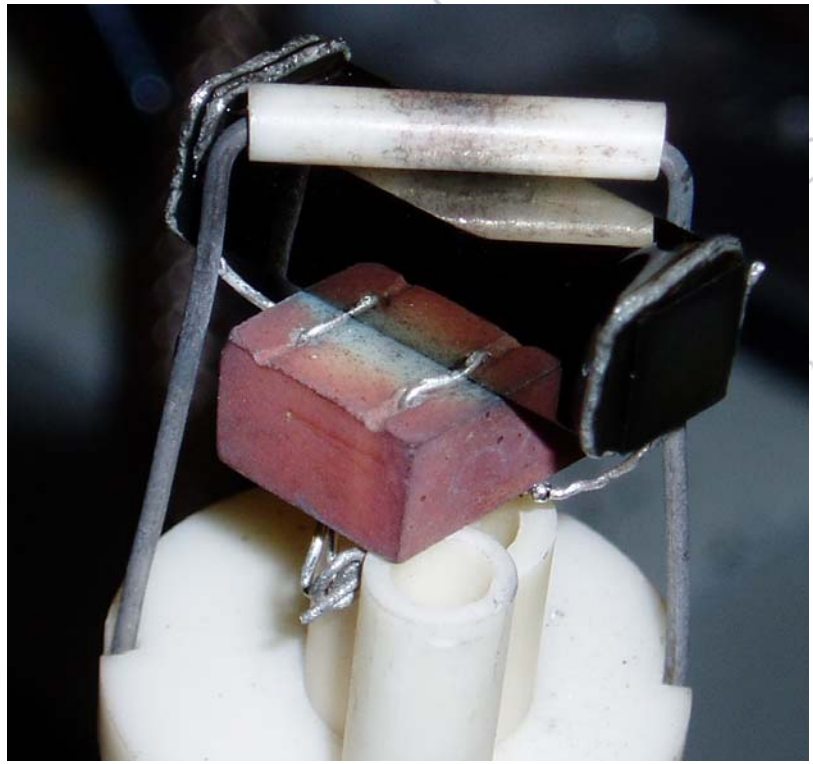
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Goal

- Goal:
  - Find oxygen stoichiometry dependence on temperature and P_{O_2} for $CeNbO_{4+d}$
  - Determine ionic and electronic conductivity
  - Calculate D_{chem} (bulk diffusion coefficient) and k_{chem} (surface exchange coefficient for O_2) values from conductivity measurements
  - Determine defect chemistry from the above results

Synthesis

- Solid state synthesis:
  - $CeNbO_{4+\delta}$ was produced by mixing CeO_2 and Nb_2O_5 that was ball milled over night and then formed into bars
  - Bars were then isostatically pressed at 2 kbar and sintered at 1400°C for 32 hours (96-98% dense after sintering)
  - Bar made for conductivity experiments was polished to a 3μm finish



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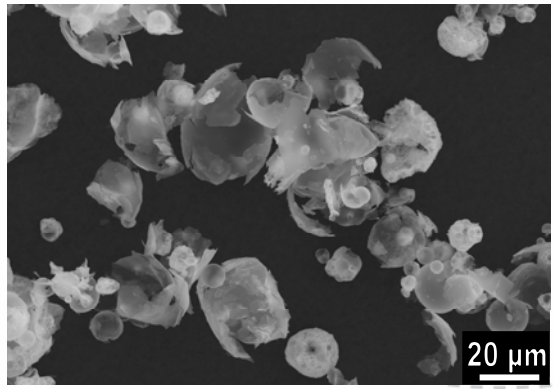
Synthesis

- $CeNbO_{4+\delta}$ powder made by wet chemistry
  - Separate solutions were made of Nb-malic acid and Ce-citric acid
  - Solutions were mixed and processed by spray pyrolysis
  - Resulting powder was heat treated at 1200°C to form $CeNbO_{4+\delta}$

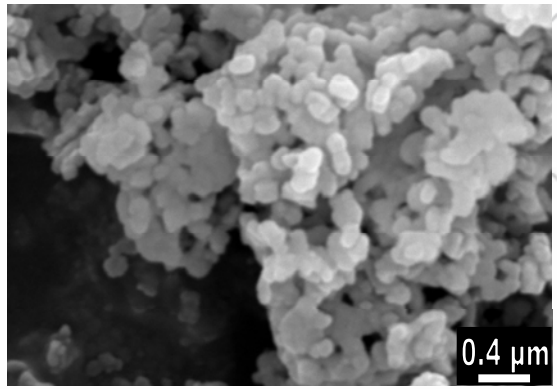


Powder characterization

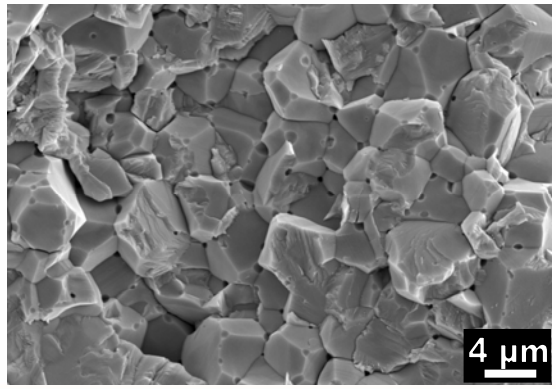
- As-synthesized powder from spray pyrolysis:
  - large, soft, spherical agglomerates
  - mainly oxide phase with limited residual carbonate and nitrate phase



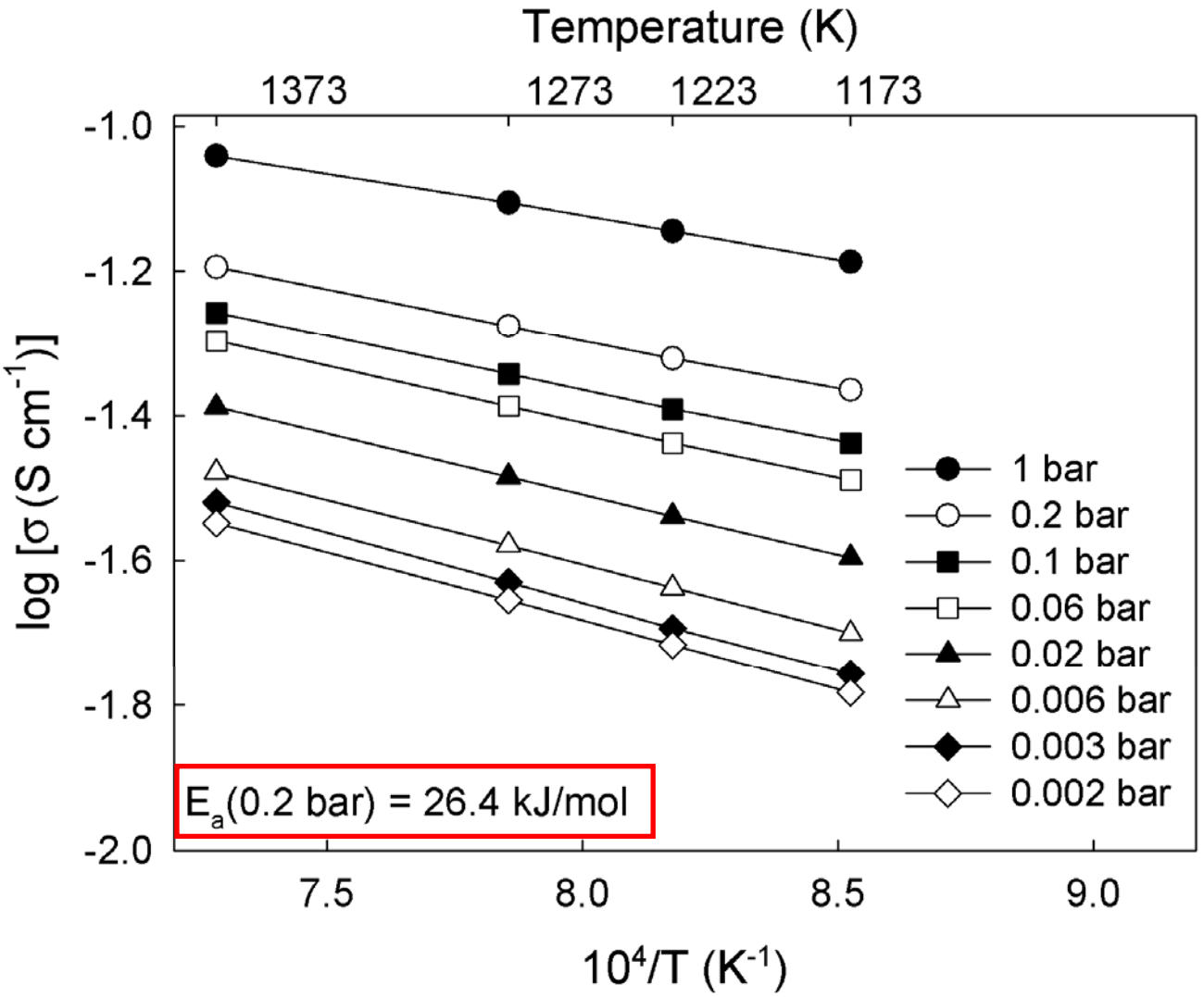
- Calcined and milled overnight
  - small particles (nano-scale)
  - phase pure powder
  - excellent sintering properties



- Sintering at high temperature
  - 99% density
  - fracture surface: grain size 1-6 µm



Log σ vs 1/T



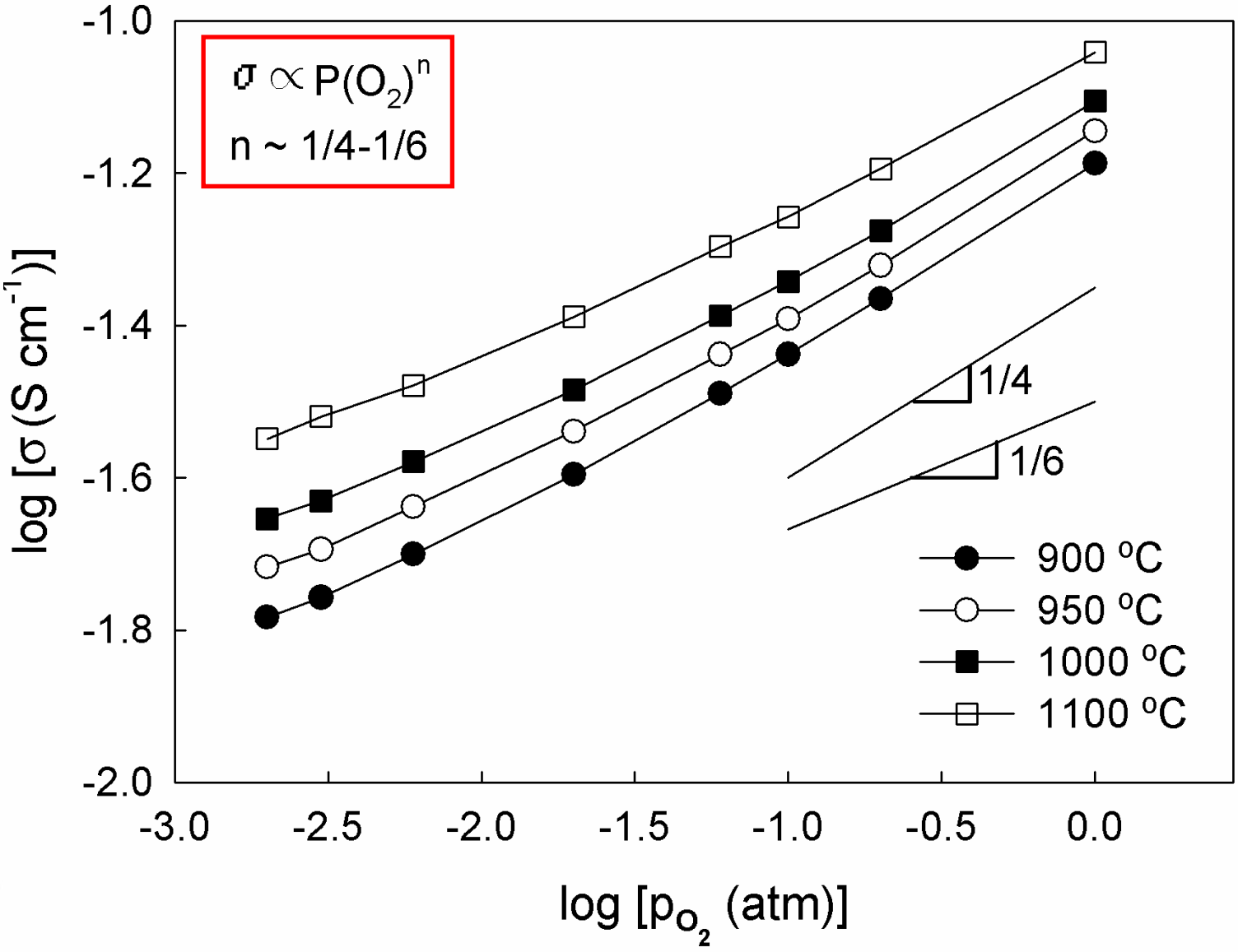
Values from litterature (E.V. Tsipis et al., *Solid State Ionics*, 177, 1015-1020 (2006) :

Ea_{ionic}(air) = 35 kJ/mol

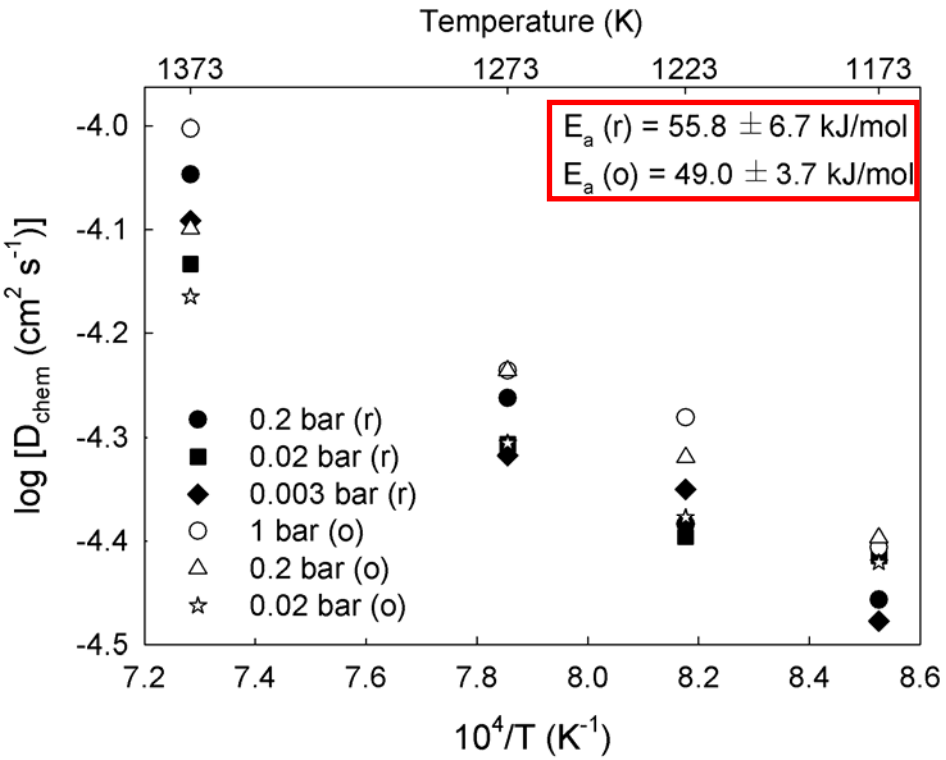
$Ea_{electronic}$(air) = 52 kJ/mol

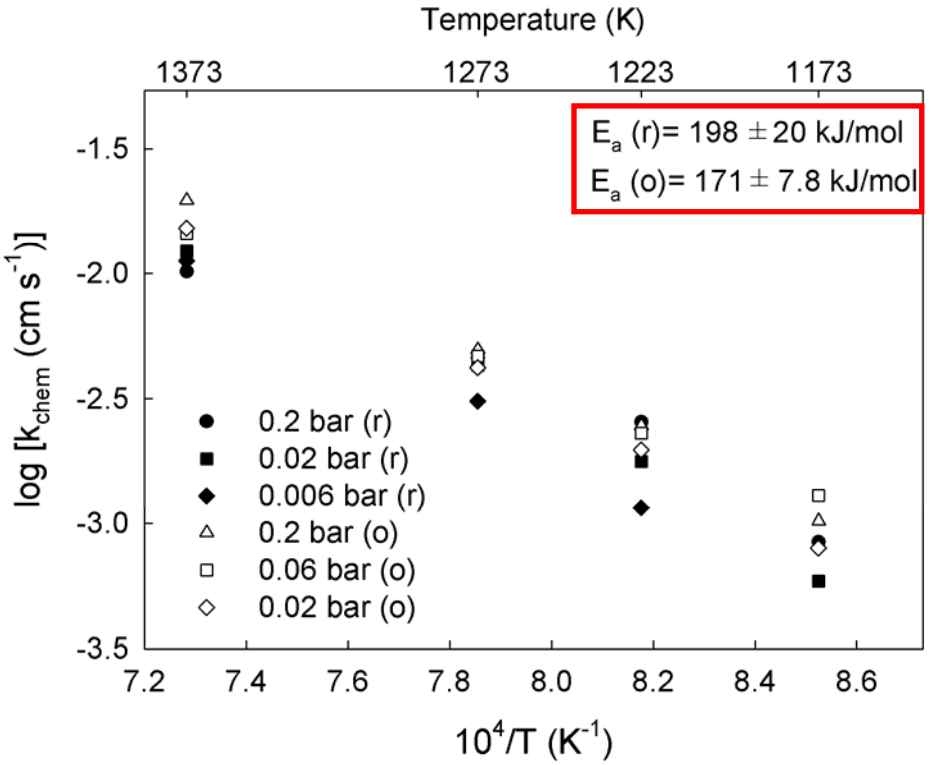
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Log(σ) vs Log(P_{O_2})

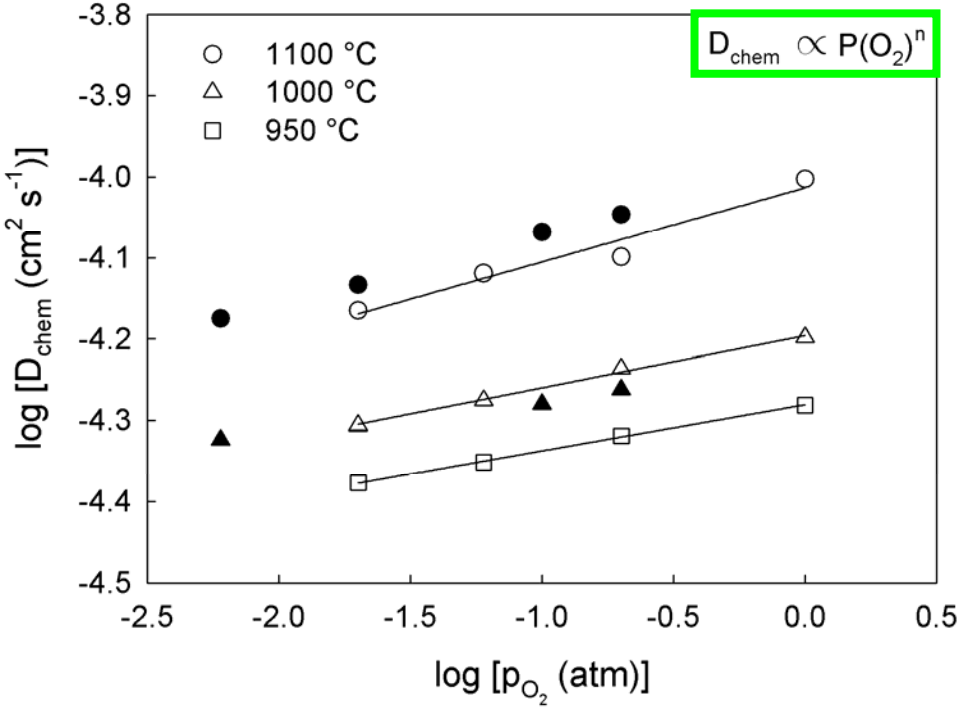


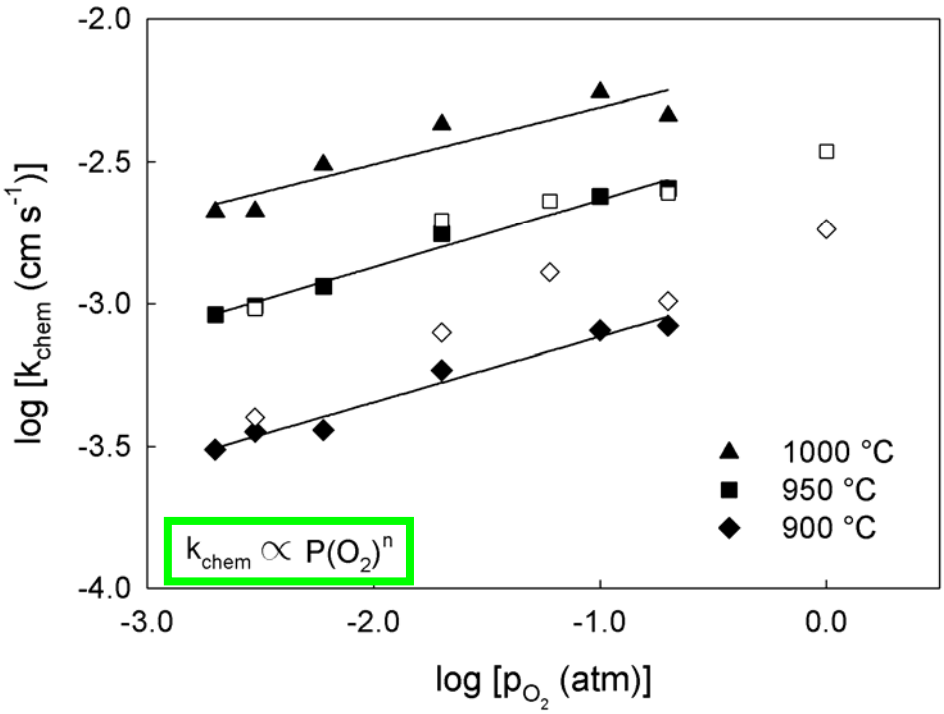
D_{chem} and k_{chem} vs $10^4/T$





D_{chem} and k_{chem} as functions of P_{O_2}





	n (red)	n (ox)
1100 °C	1/12	1/11
1000 °C	1/25	1/16
950 °C	-	1/18

	n (red)	n (ox)
1000 °C	1/5	-
950 °C	1/4	1/5
900 °C	1/4	1/4

Defect chemistry for $CeNbO_{4+\delta}$

$$\frac{1}{2}O_2(g) \rightarrow O_i'' + 2h^{\bullet}$$

$$K = \frac{[O_i''][h^{\bullet}]^2}{P_{O_2}^{1/2}}$$

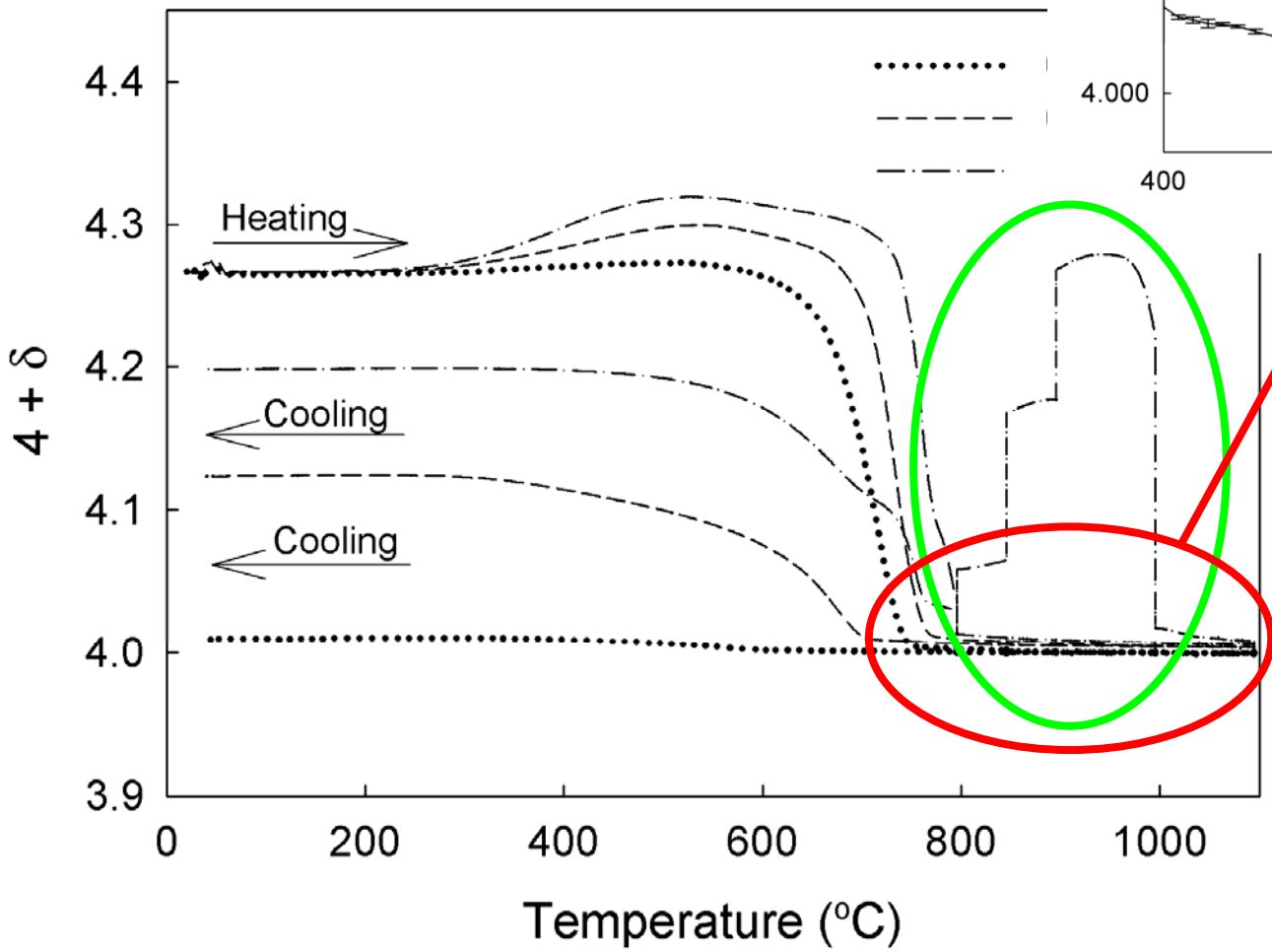
$$[h^{\bullet}] \propto P_{O_2}^{1/6} \Rightarrow \sigma \propto P_{O_2}^{1/6}$$

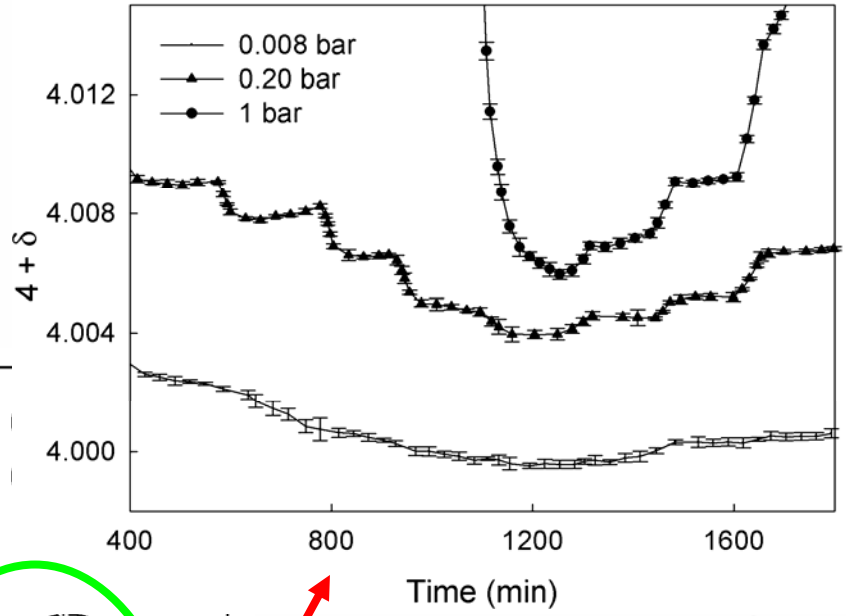
If electron holes is the majority charge carrier, it is expected that the line describing the dependence of conductivity on $\log P_{O2}$ would be close to 1/6.

The slope of the line in the current study is approximately 1/5, meaning that there are other defects contributing to the total conductivity as well.

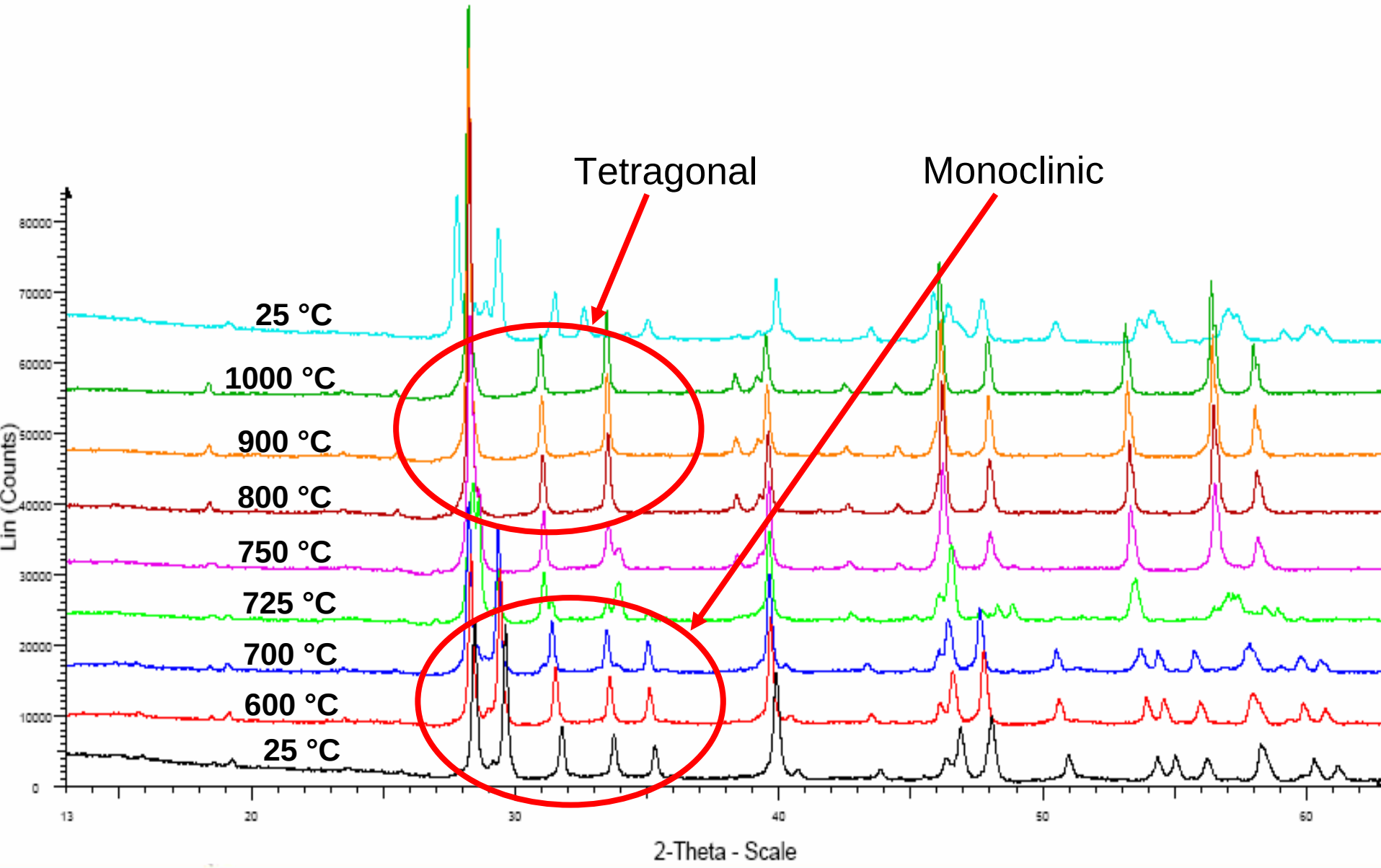
TGA in air of $CeNbO_{4+\delta}$

- Heat treatment history:
  - 2x3 hours at 800 °C
  - 50 hours at 1200 °C

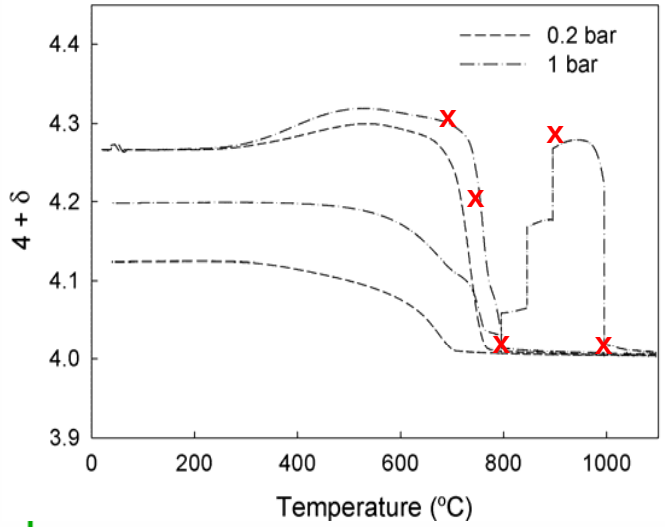


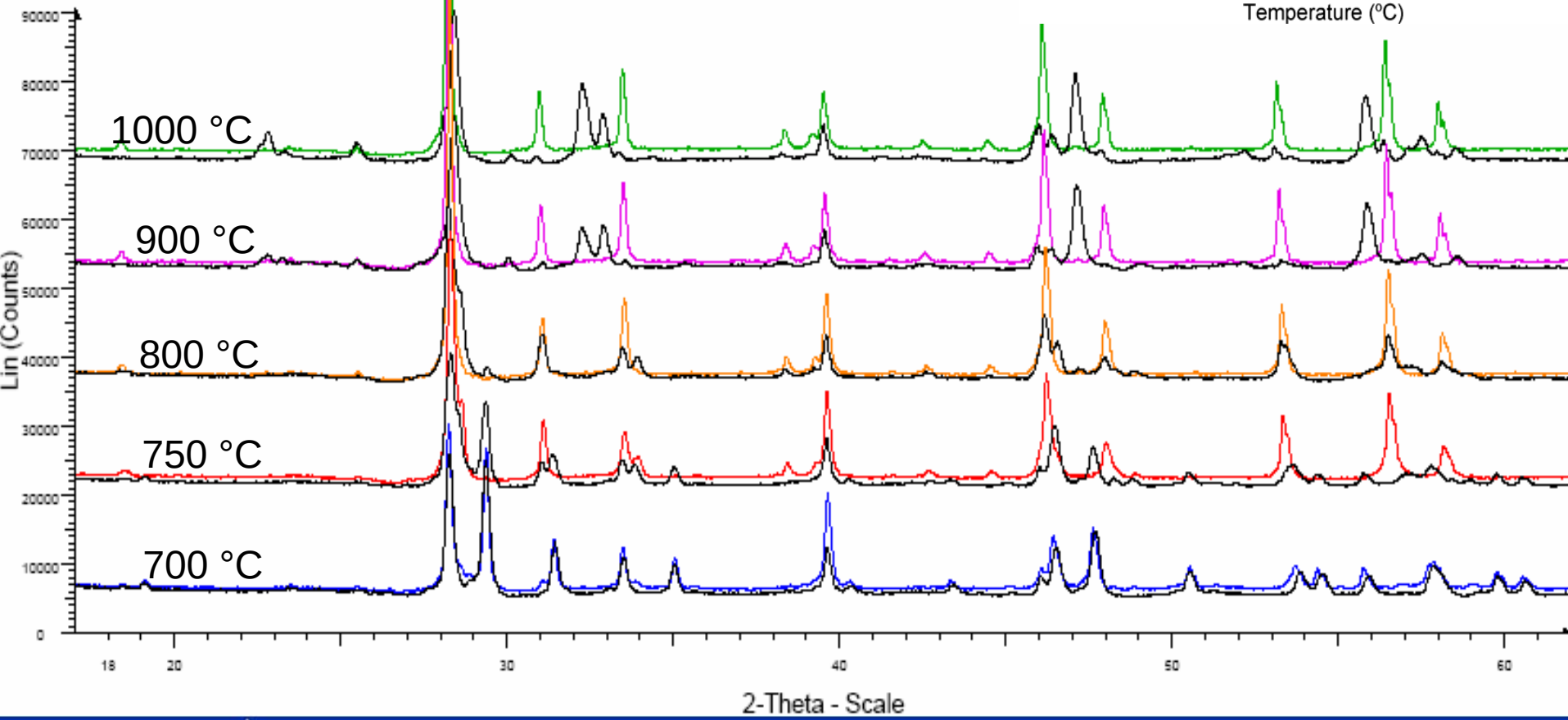


$CeNbO_{4+\delta}$ in air

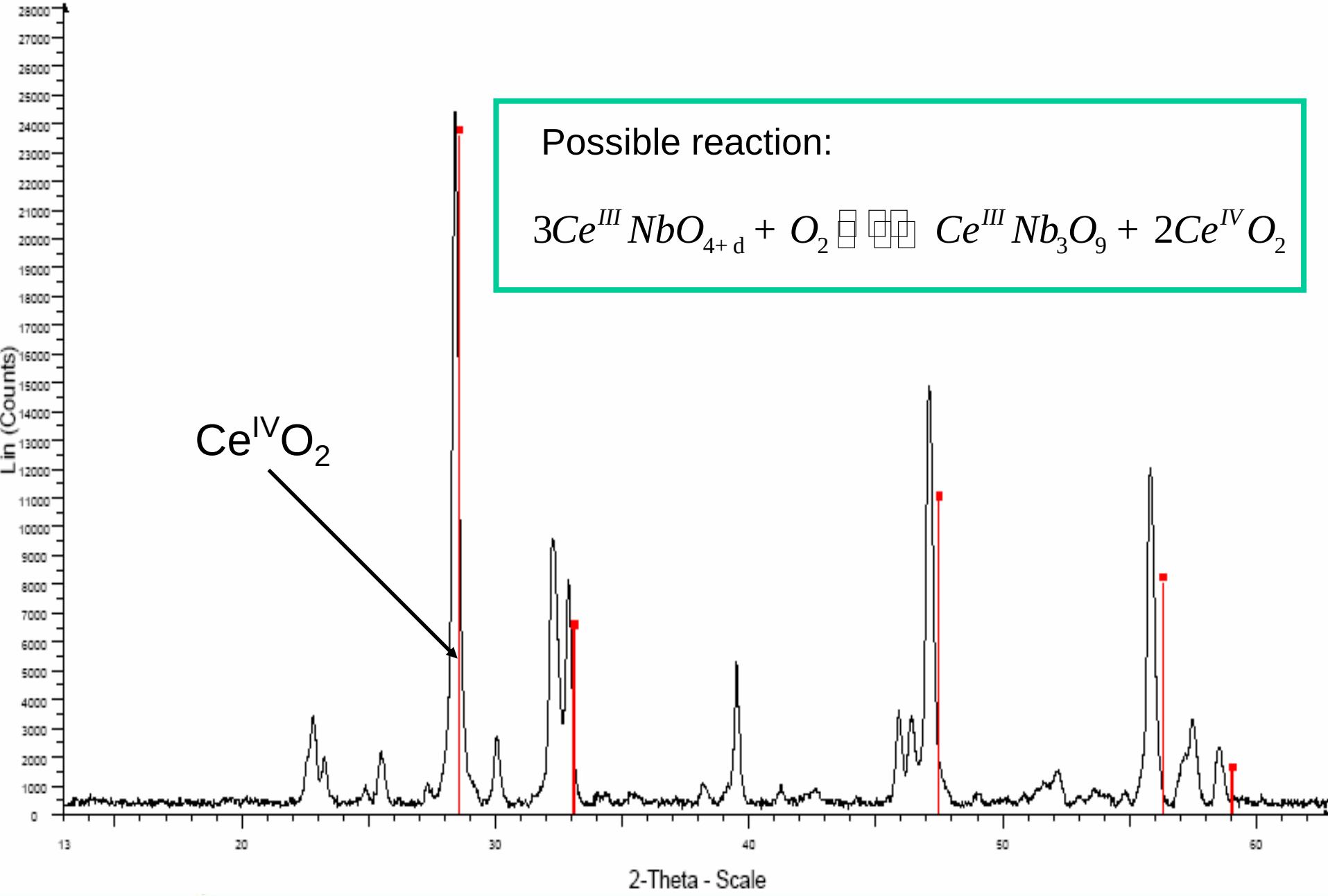


$CeNbO_{4+\delta}$ in air and O_2





HTXRD CeNbO4+d at 960 °C



Possible reaction:

$$3Ce^{III}NbO_{4+d} + O_2 \rightarrow Ce^{III}Nb_3O_9 + 2Ce^{IV}O_2$$

Summary

- Dense $CeNbO_{4+\delta}$ show conductivities ranging from $9{,}1 \cdot 10^{-2}$ S/cm at 1100 °C and 100% O_2 to $1{,}7 \cdot 10^{-2}$ S/cm at 900 °C and 0,2% O_2.
- Results suggest a mixed ionic and electronic conductivity due to the formation of oxygen interstitials and electron holes.
- At higher temperatures (1000-1100 °C) bulk diffusion seems to be controlling, while at lower temperatures (900 °C) the surface exchange rate is the limiting factor.
- HTXRD showed different behavior in air and O_2 upon heating. Most likely due to a decomposition of $Ce^{III}NbO_{4+\delta}$ to $Ce^{III}Nb_3O_9$ and $Ce^{IV}O_2$.