Surface species and interactions between adsorbed chloride and water on stored PuO_2

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DISTINCTIVE

Contents

- Background.
- Recap from poster at DISTINCTIVE AGM.
- Recent results.
- Future work.

Why?

- 5% of 100 tonnes PuO_2 known to be contaminated with 14,000 ppm Cl^- and 0.5-2% H_2O.
- Must be decontaminated for either reuse or safe disposal.
- Understand how it behaves and evolves over time.
- Develop heat treatment method with no caustic aqueous waste.[1]

1 C. Campbell, C. Gregson, R. Orr, H. Sims, R. Taylor and K. Webb, *NNL, National Nuclear Laboratory, Sellafield*, 2014, **12869**, 1–68.

CeO_2

- Non-toxic and non-radiotoxic substitutes avoid dangerous lab work.
- +4 oxidation state.
- CeO_2, ThO_2 and UO_2.[2]
- Different elements can produce different spectra.

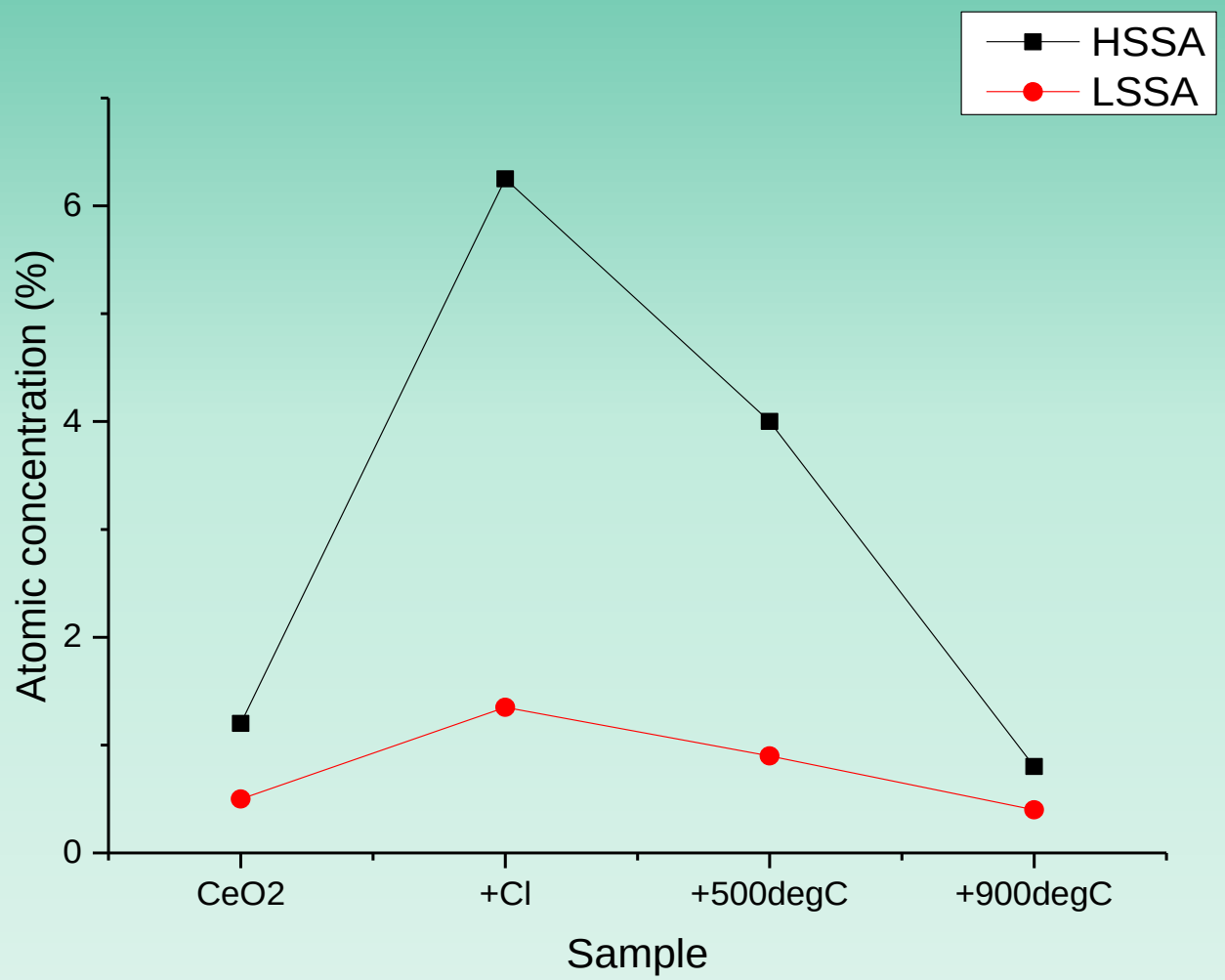
2 P. Martin, M. Ripert, T. Petit, T. Reich, C. Hennig, F. D'Acapito, J.L. Hazemann and O. Proux, *Journal of Nuclear Materials*, 2003, **312**, 103-110.

Materials and methods

Batch	Manufacturer	High/Low Specific Surface Area	CeO_2	Cl^- contamination	Heat treatment at 500 °C	Heat treatment at 900 °C
1	NNL	HSSA	✓	✓	✓	✓
1	NNL	LSSA	✓	✓	✓	✓
2	Sophie	HSSA	✓	✓	X	X
2	Sophie	LSSA	✓	✓	X	X

- Batch 1 HSSA = 58 $m^2\ g^{-1}$ and LSSA = 2 $m^2\ g^{-1}$.
- X-Ray Photoelectron Spectroscopy (XPS) – surface.
- X-Ray Diffraction (XRD) – bulk.
- Infrared Spectroscopy (IR) – functional groups.
- Scanning Electron Microscopy (SEM) – images.
- Energy Dispersive Spectroscopy (EDS) – elemental detection.
- Focussed Ion Beam (FIB) – sectioning.
- Transmission Electron Microscopy (TEM) – images.

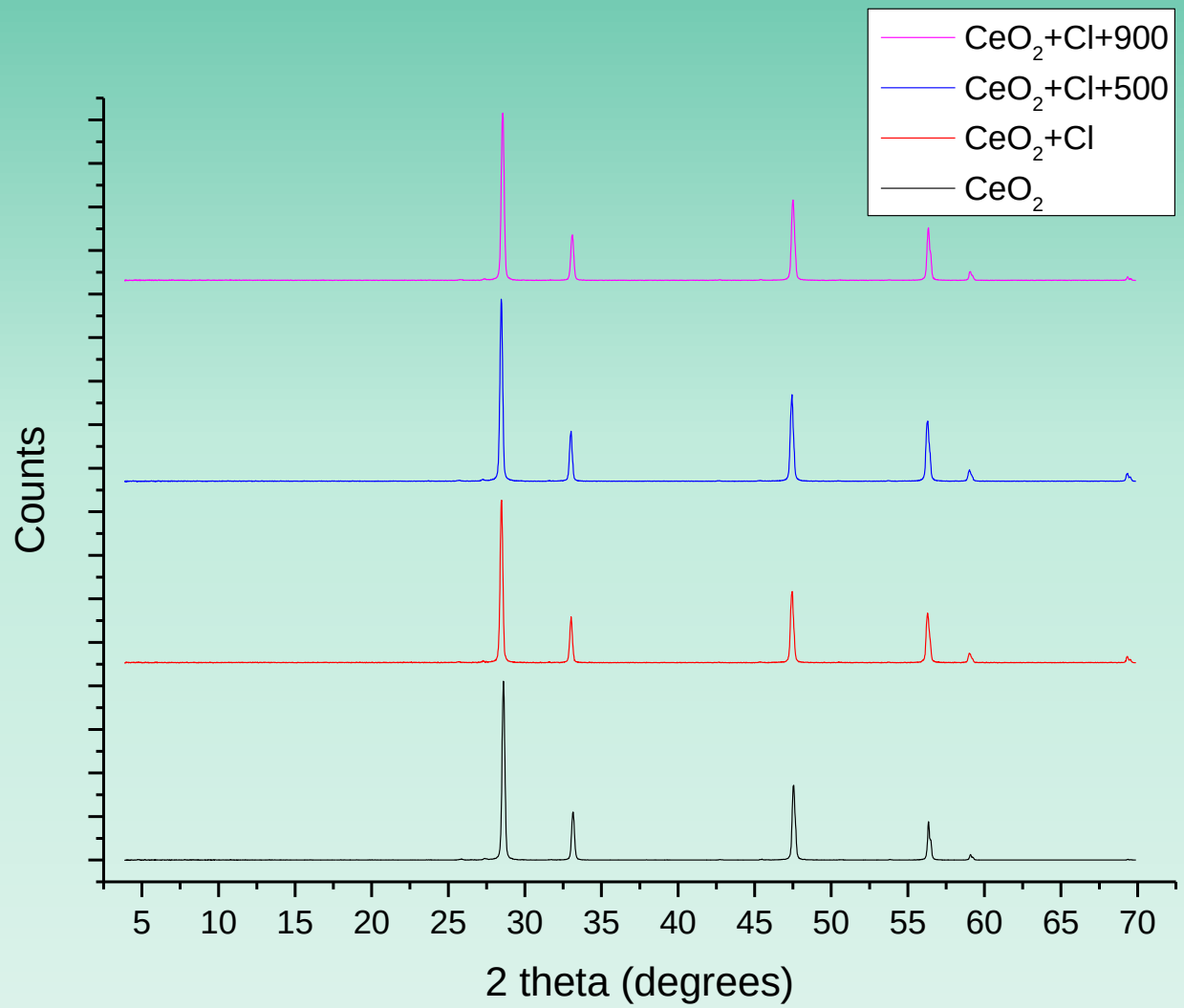
Recap (Batch 1 XPS)



- HSSA particles adsorb more Cl^- than LSSA.
- Heat treatment removes more Cl^- from HSSA than LSSA particles, but not all.

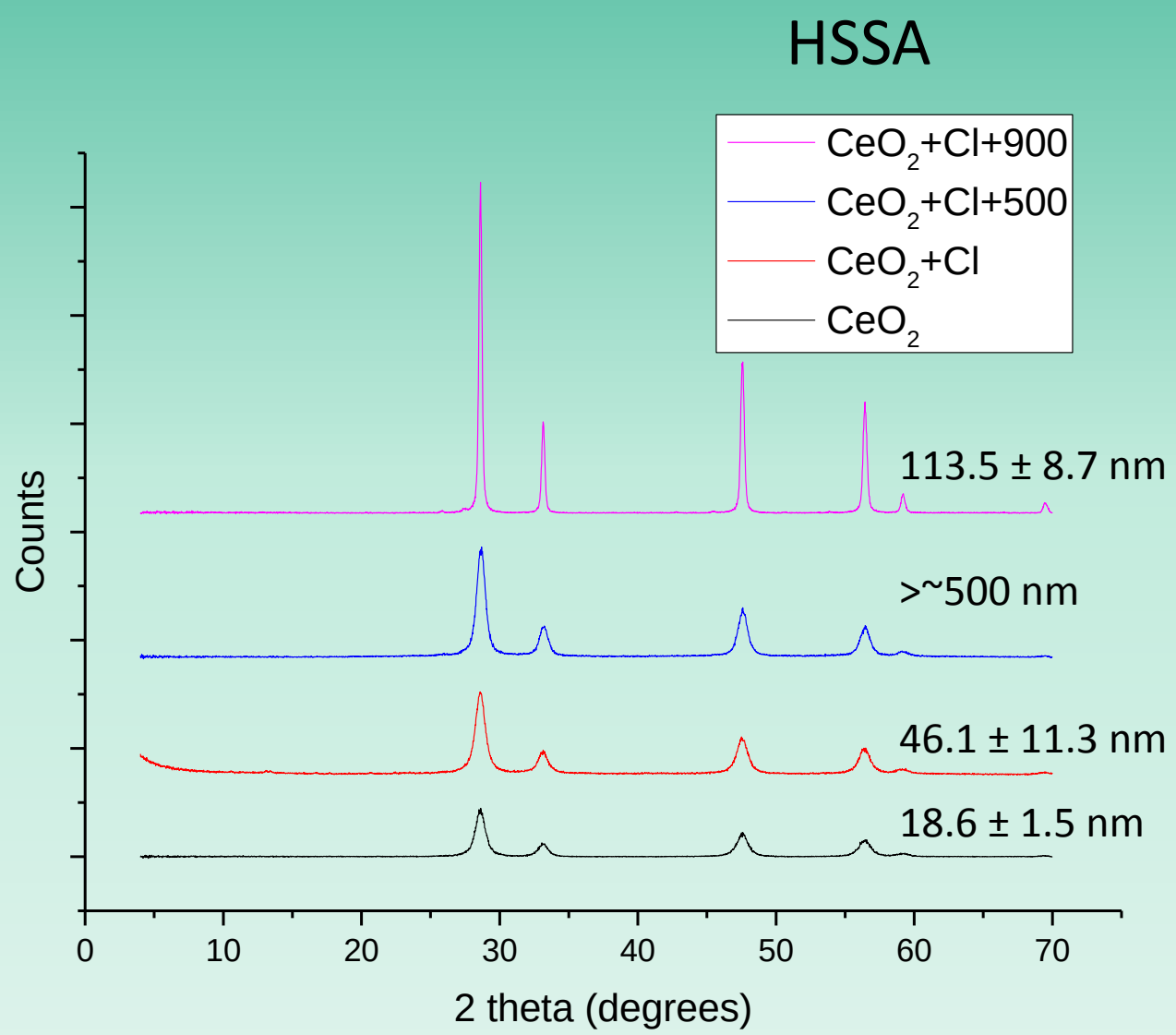
Recap (Batch 1 XRD)

LSSA



- Contaminating CeO_2 with Cl^- does not significantly affect its structure.
- Little gained from heat treating LSSA at 900 °C than 500 °C to remove Cl^-.
- Can't measure particle sizes – peaks are too narrow.

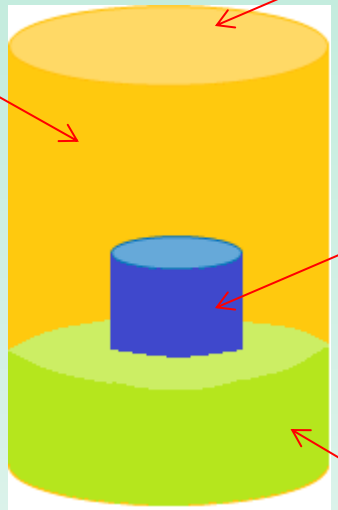
Recap (Batch 1 XRD)



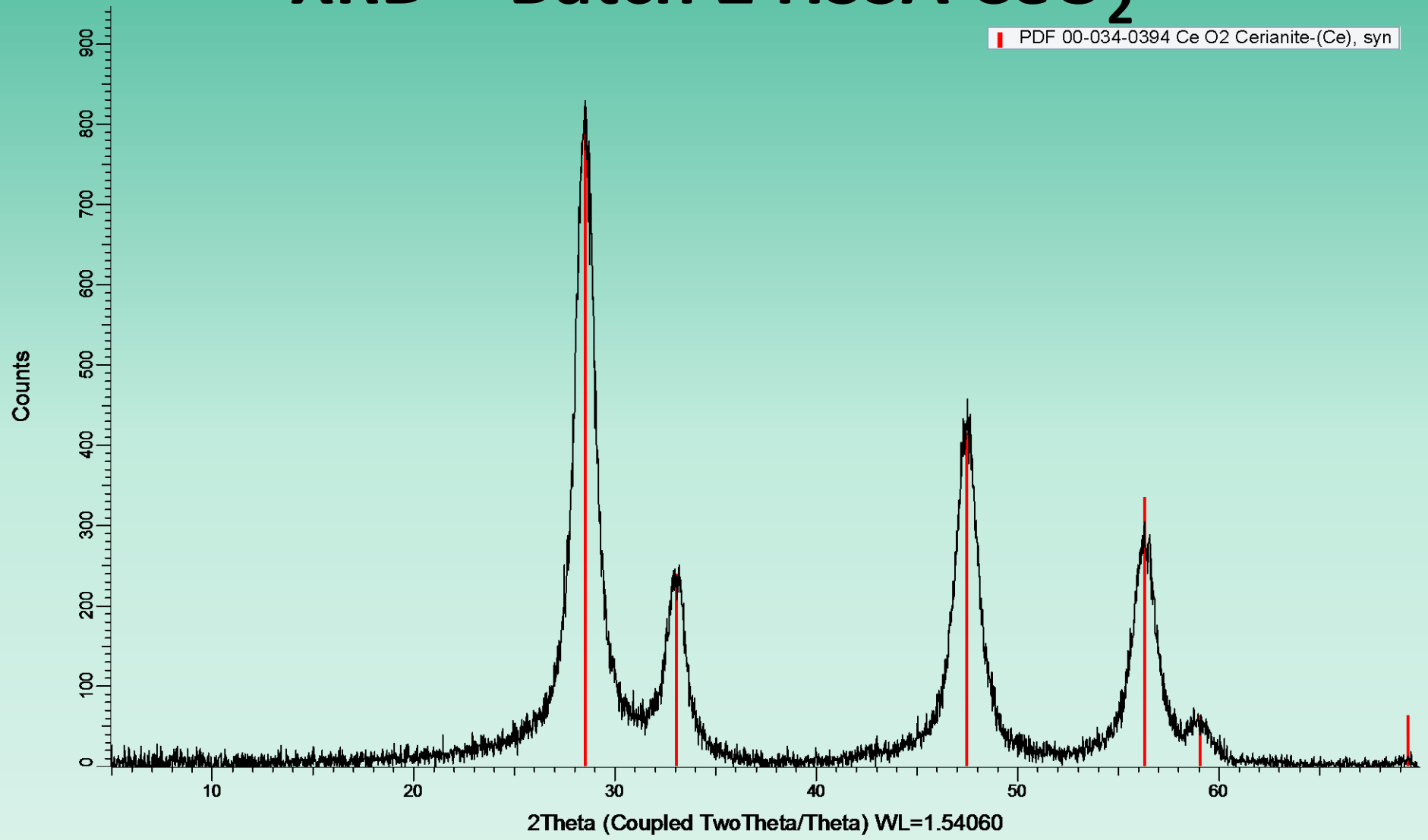
- Crystal size increases with Cl^--contamination.
- Not due to change in CeO_2 over time – Cl^- effect.
- Heat treating HSSA particles above 500 °C greatly increases crystal size.
- Possible physical entrapment of Cl^- within pores.

Synthesis

1. Oxalate precipitation at 25 °C.
2. Cerium oxalate calcination at 900 and 500 °C => LSSA and HSSA CeO_2 particles respectively.
3. CeO_2 exposed to HCl solution for 7 days for contamination.
4. Heat treatment at 500 and 900 °C.[1]

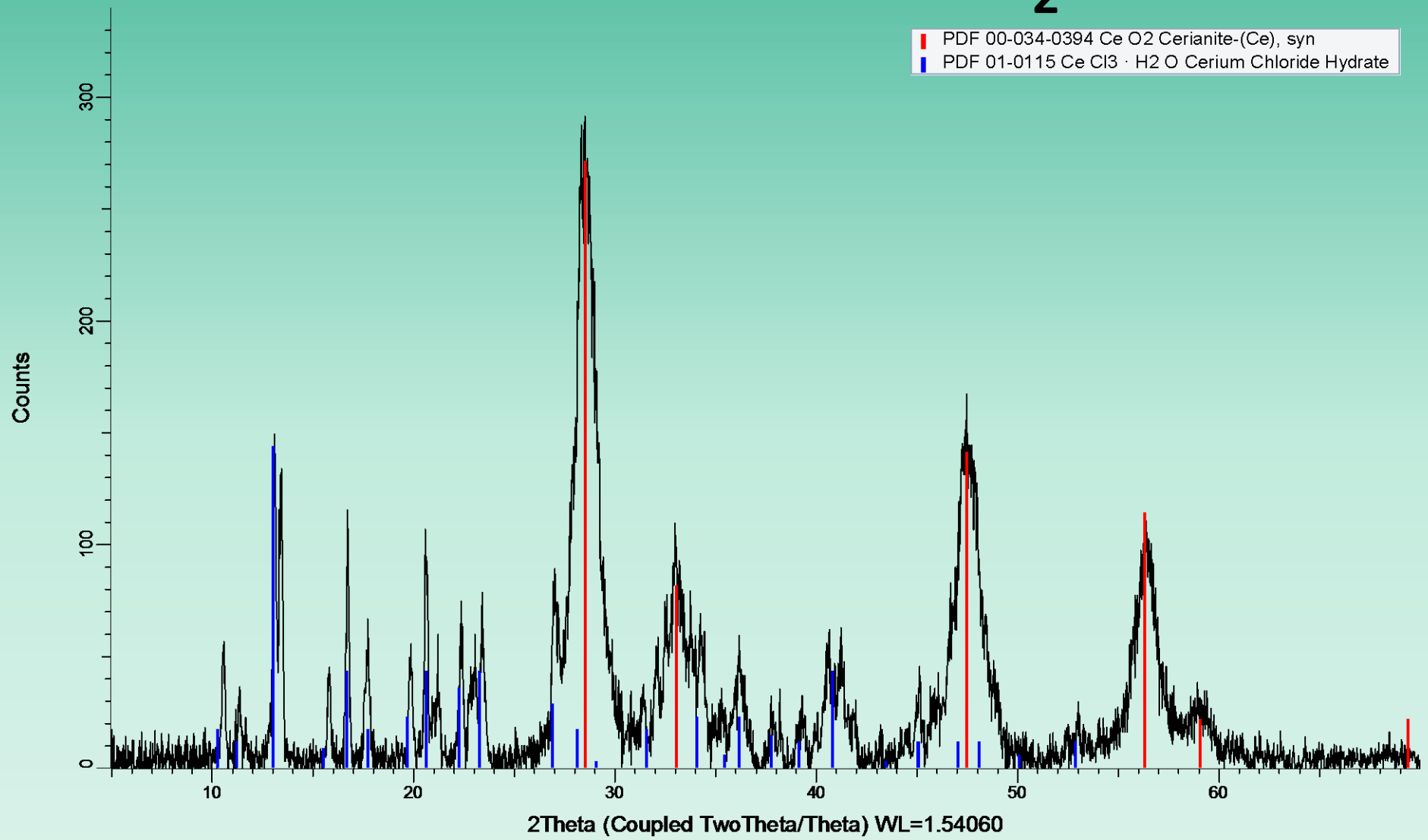


XRD – Batch 2 HSSA CeO_2



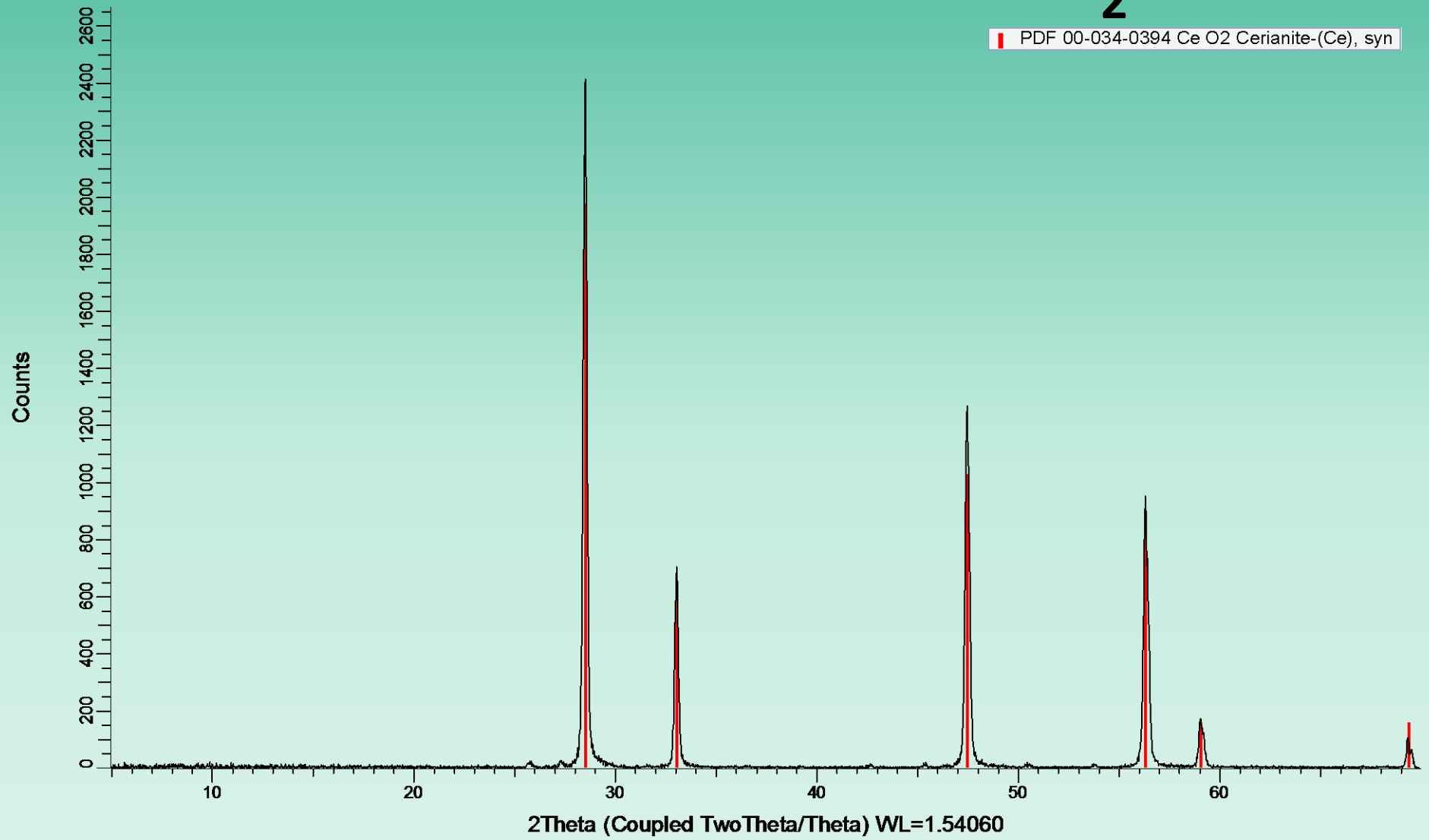
- Successfully synthesised CeO_2 nanocrystals.

XRD – Batch 2 HSSA CeO_2 + Cl^-



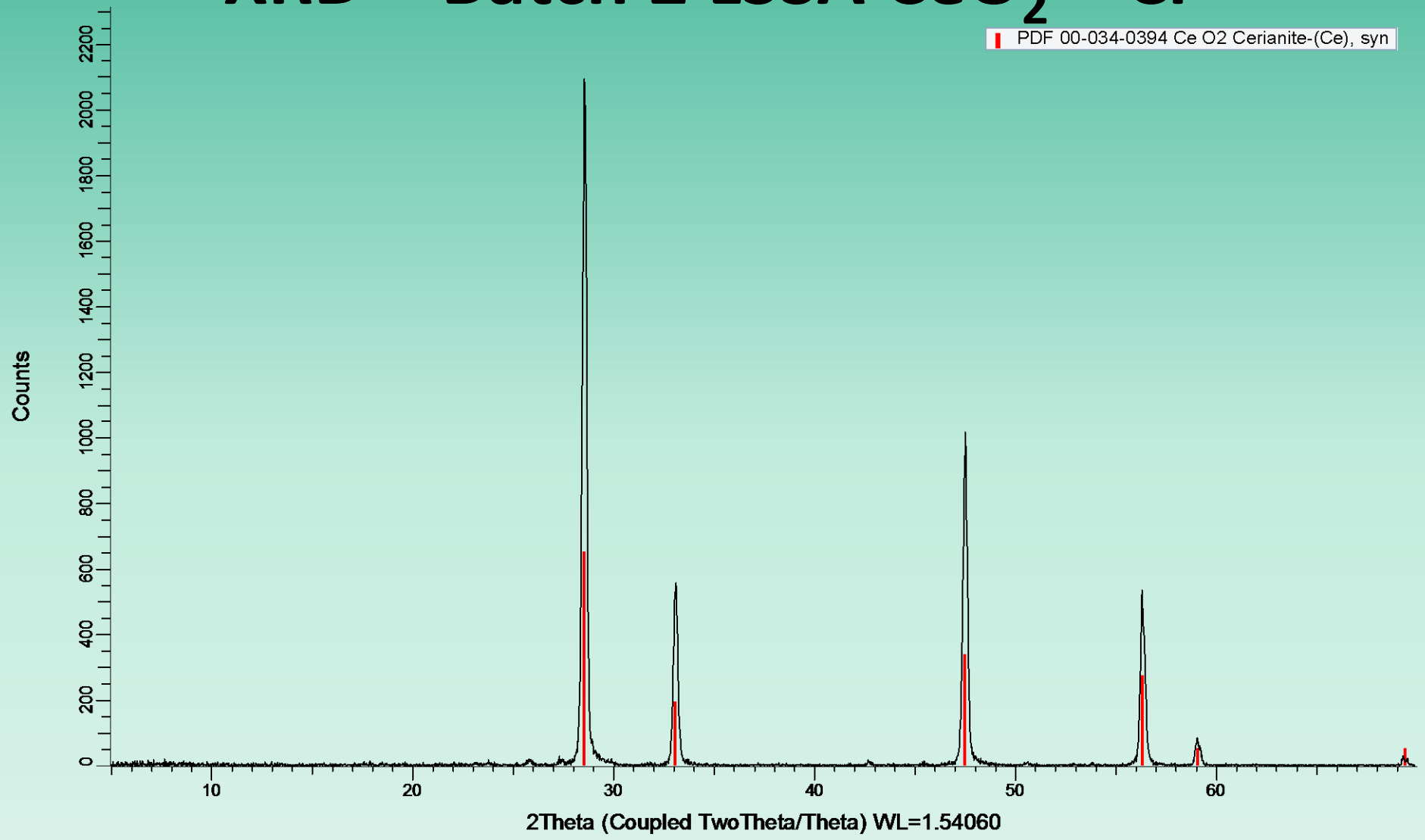
- Additional cerium chloride heptahydrate phase.
- Cl^- has been incorporated into the bulk structure.

XRD – Batch 2 LSSA CeO_2



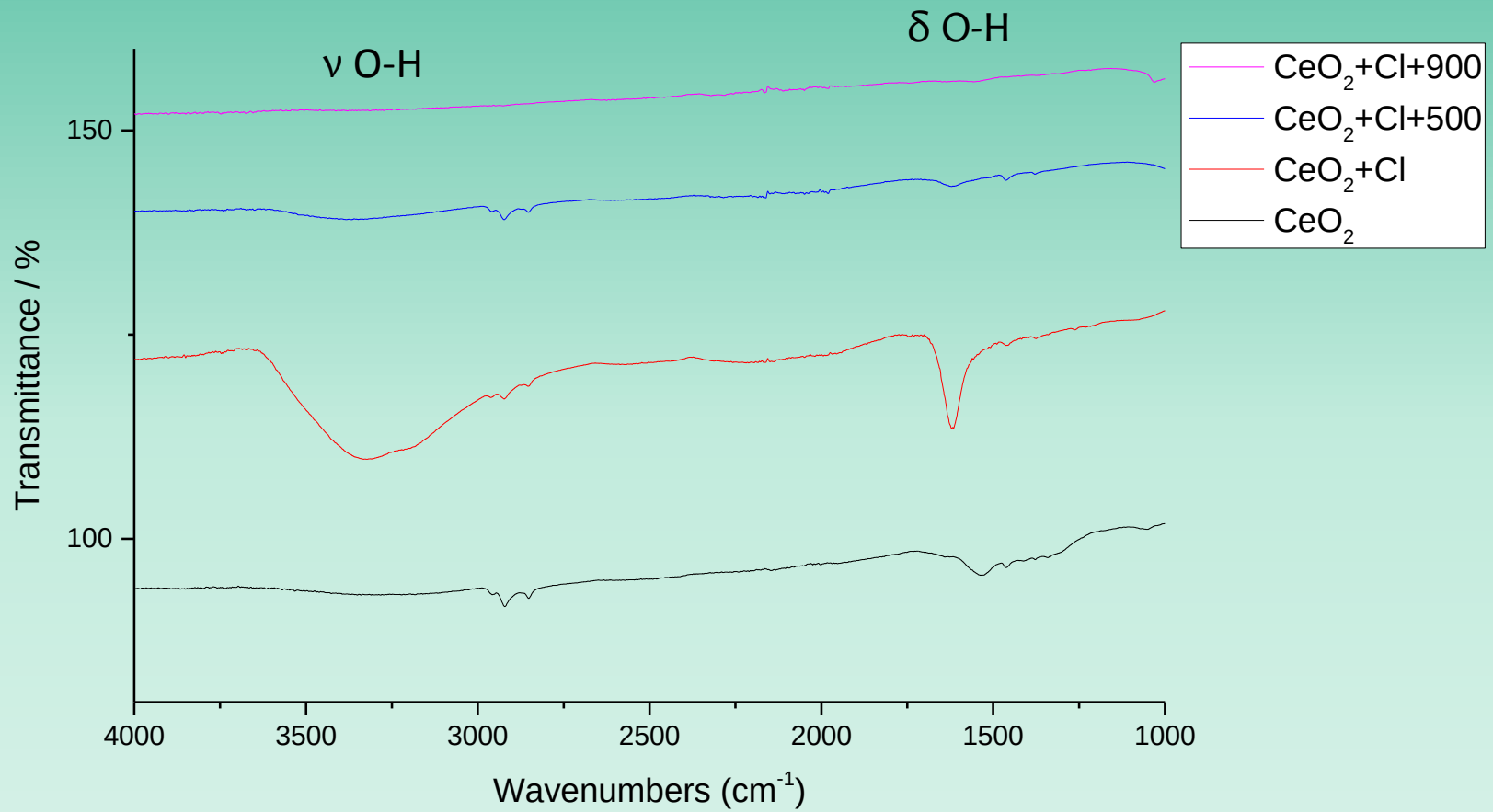
- Successfully synthesised CeO_2 microcrystals.

XRD – Batch 2 LSSA CeO_2 + Cl^-



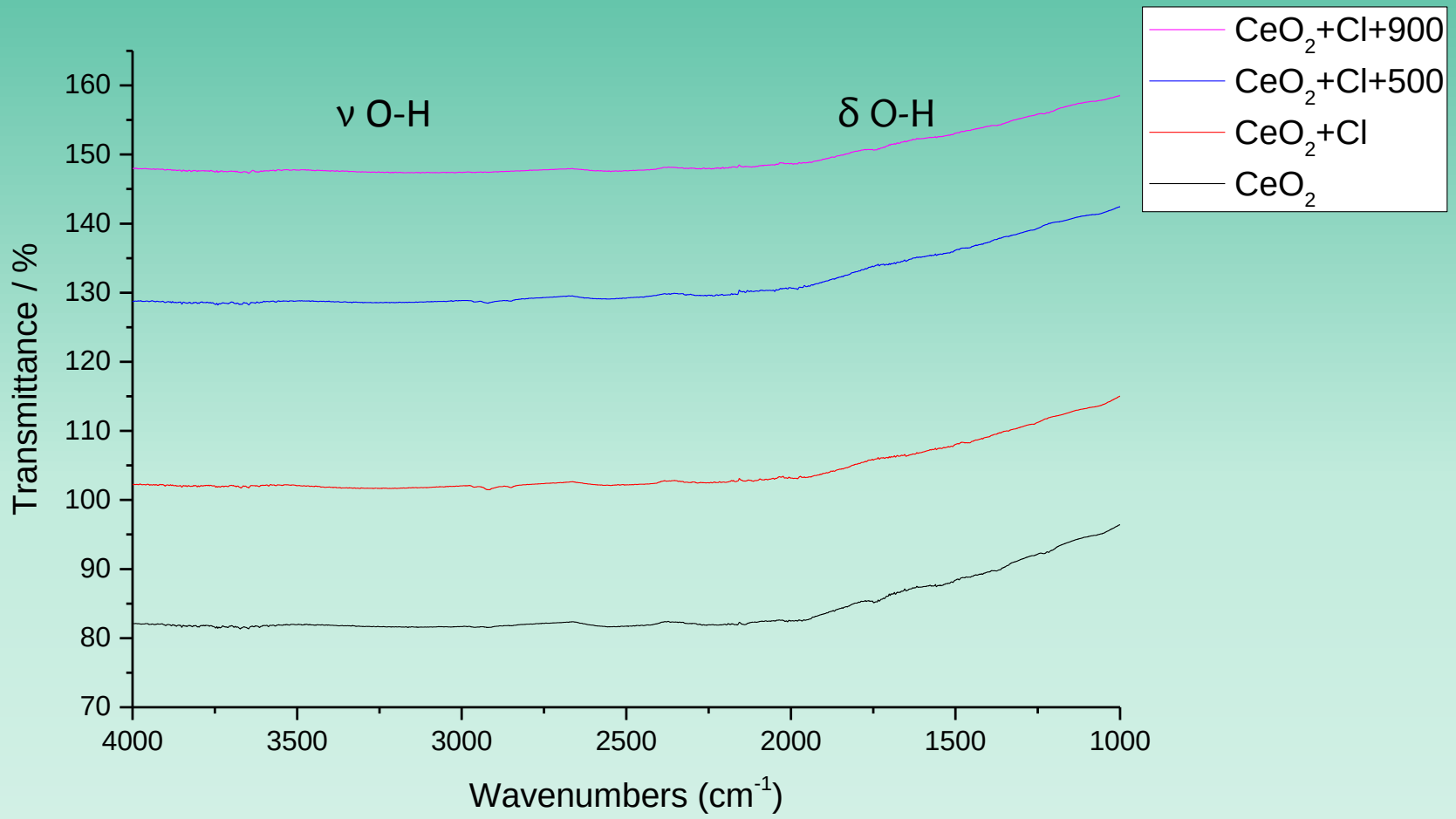
- Unlike HSSA particles, Cl^- is not incorporated into the bulk structure.

Infrared Spectroscopy – Batch 1 HSSA



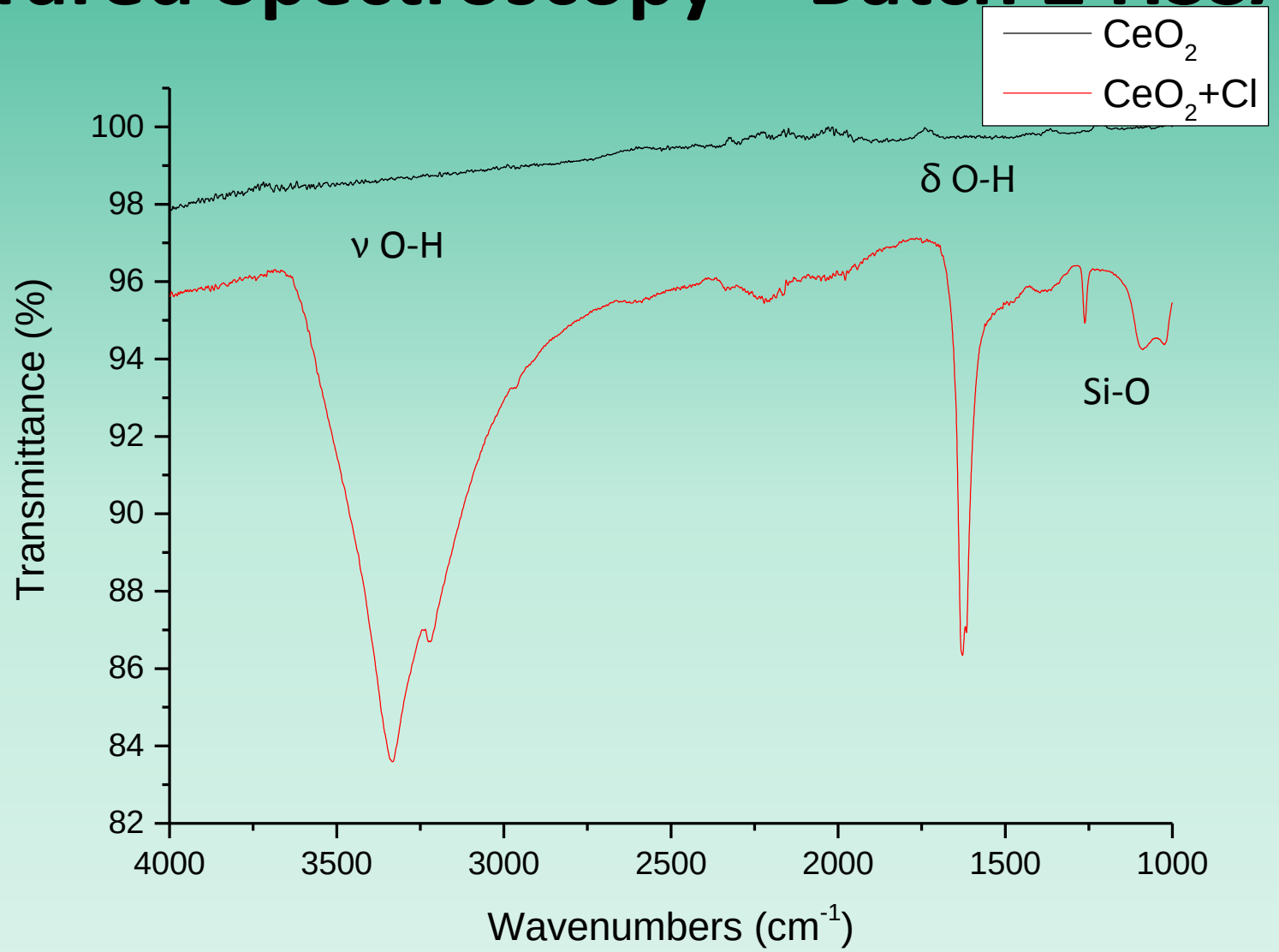
- Intensities of O-H peaks increase with contamination and decrease with heat treatment (more so at 900 than 500 °C).
- Can't use IR spectroscopy to measure Cl^-.

Infrared Spectroscopy – Batch 1 LSSA



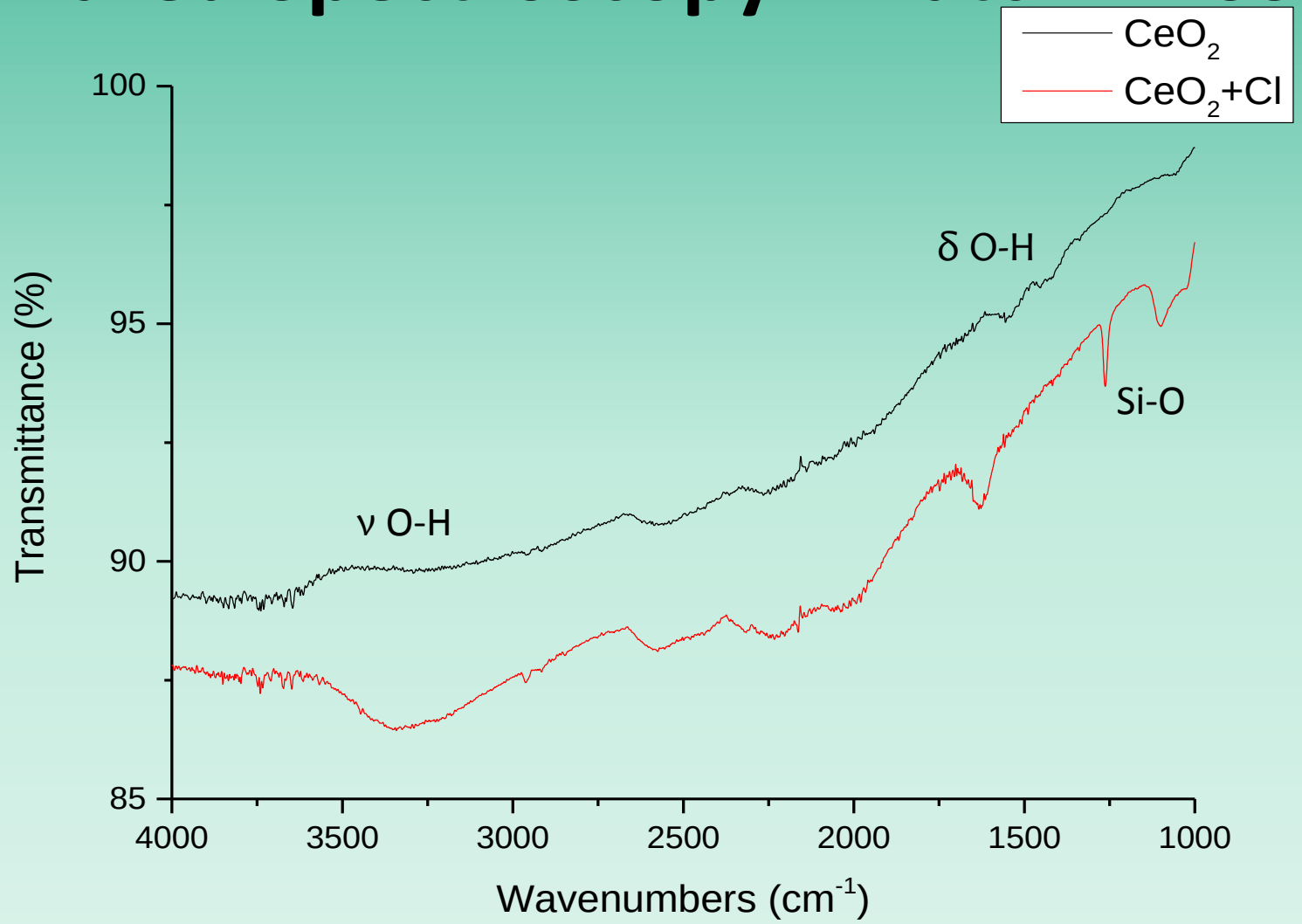
- Less difference in peak intensities for LSSA particles than HSSA.
- Less water adsorbs to and desorbs from LSSA than HSSA.

Infrared Spectroscopy – Batch 2 HSSA



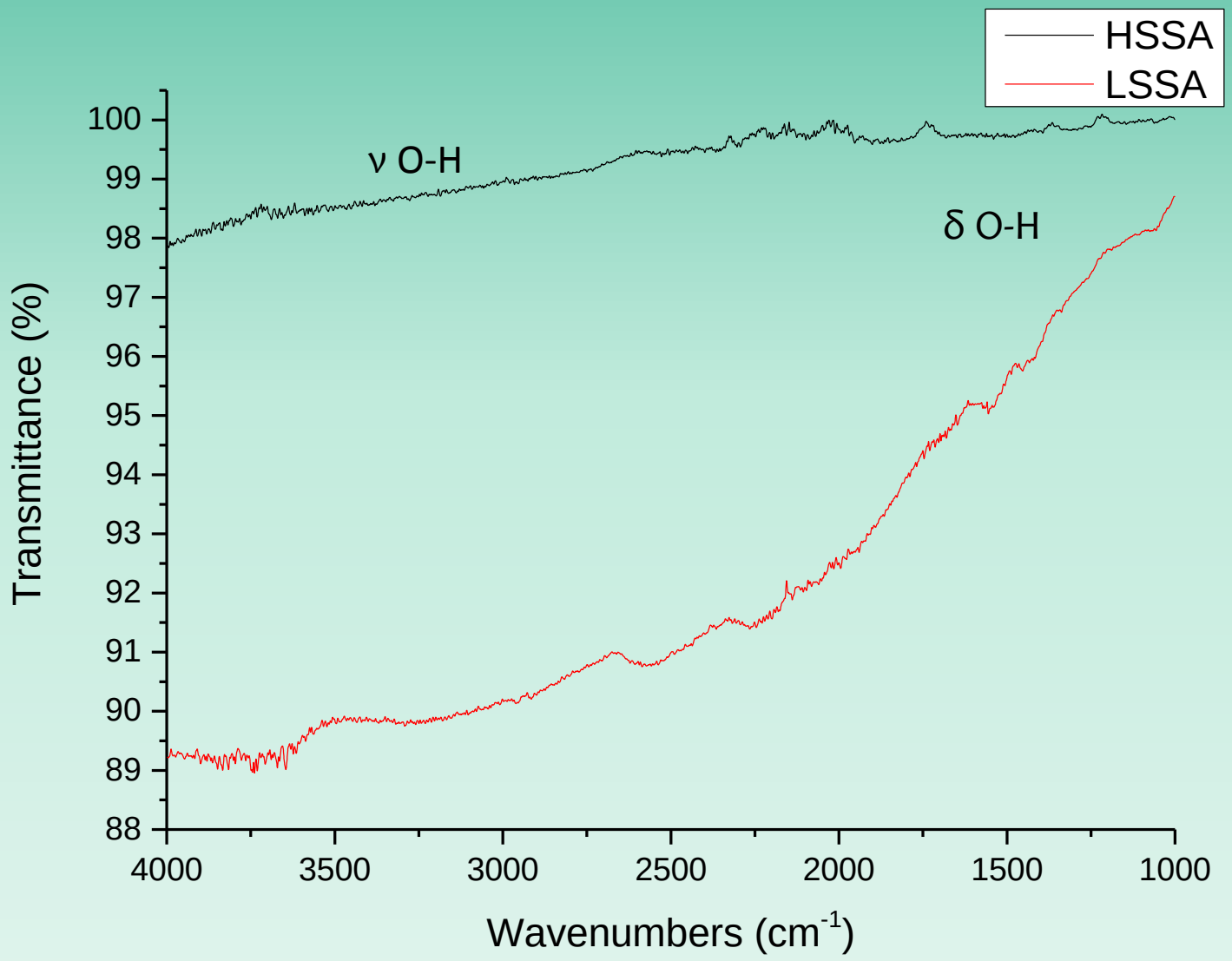
- Much more O-H than in Batch 1.
- Si-O possibly from glassware – use teflon bottles in future.

Infrared Spectroscopy – Batch 2 LSSA

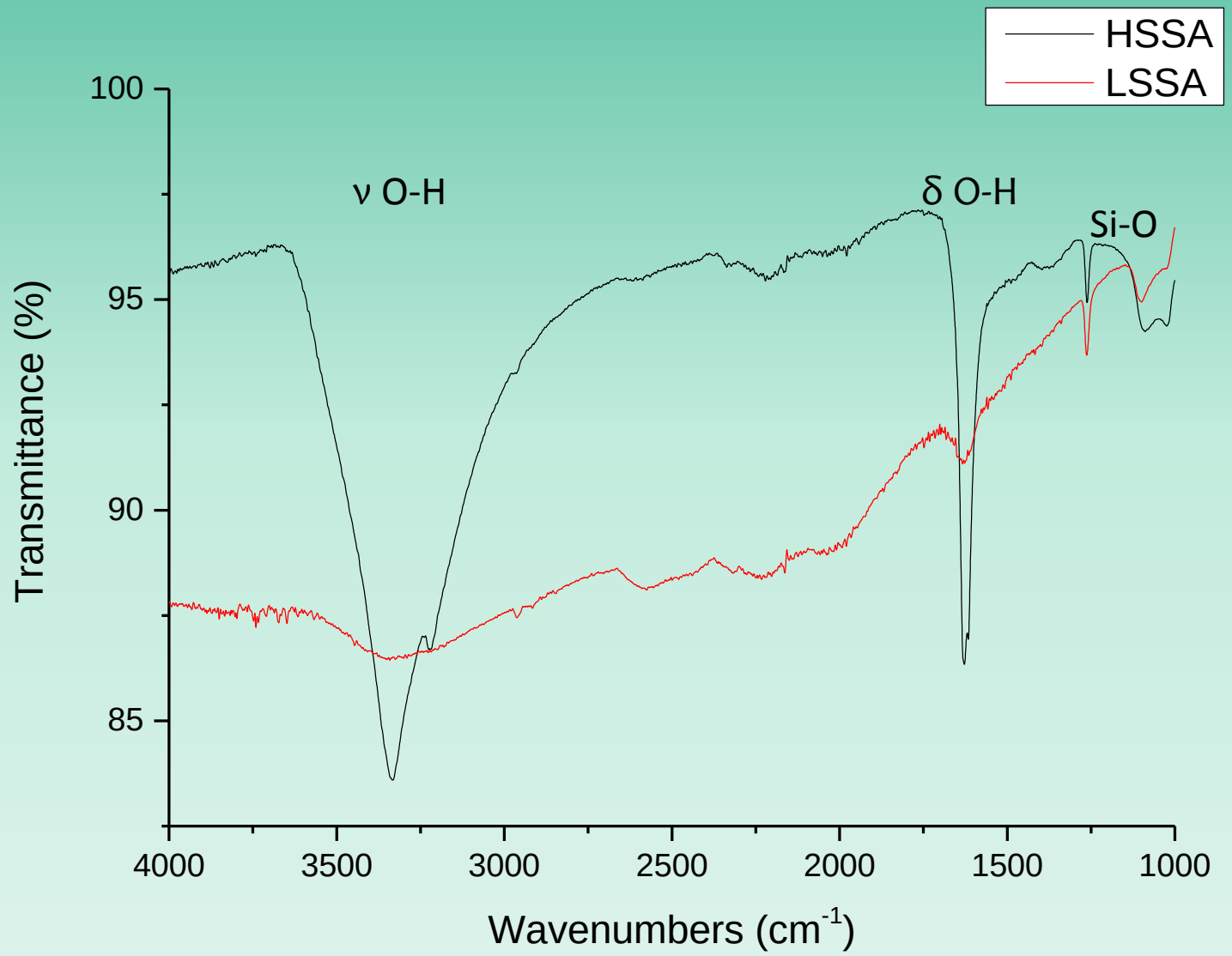


- O-H peaks more intense than Batch 1 LSSA but less than Batch 2 HSSA.

Infrared Spectroscopy – Batch 2 CeO_2

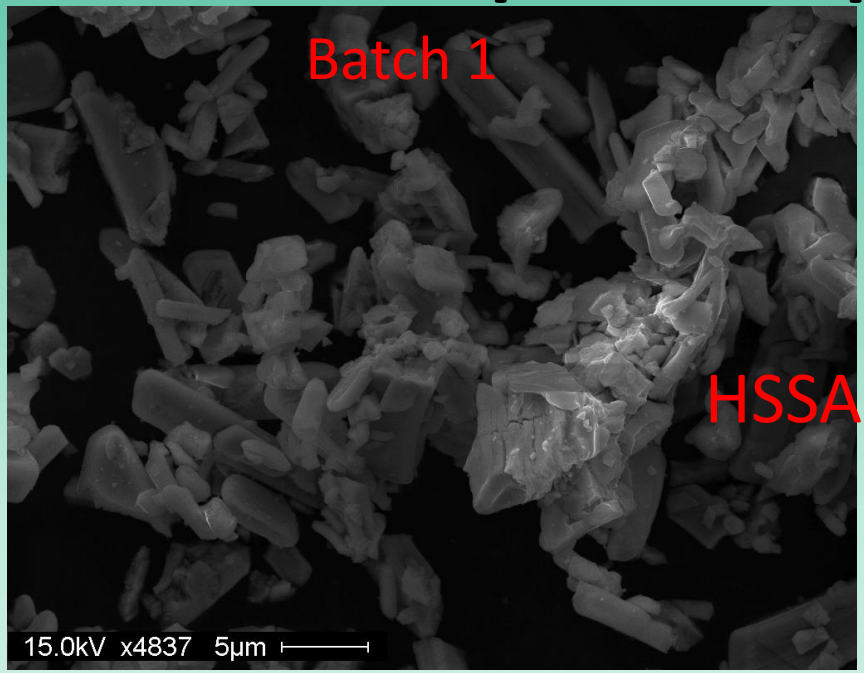


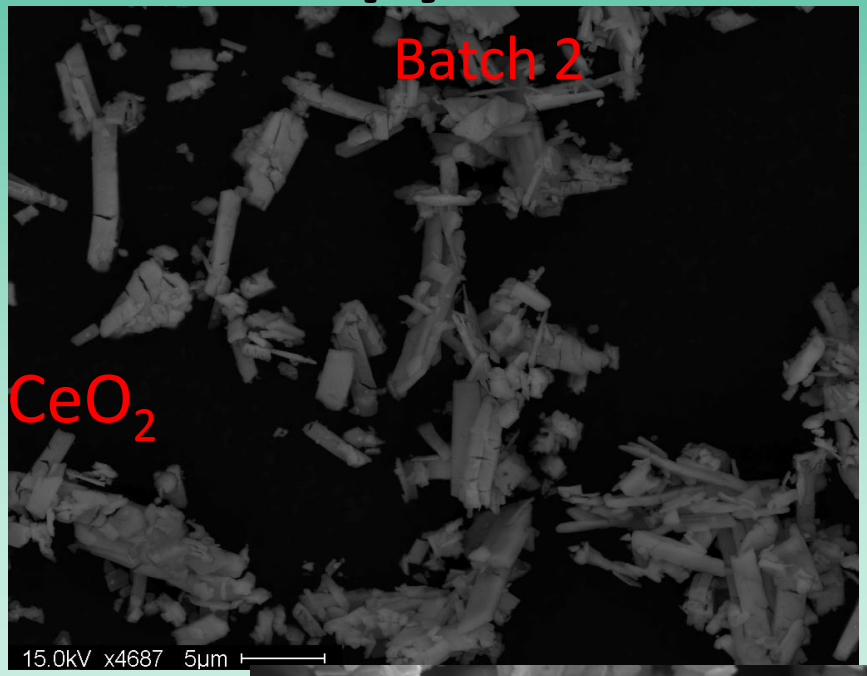
Infrared Spectroscopy – Batch 2 CeO_2+Cl^-



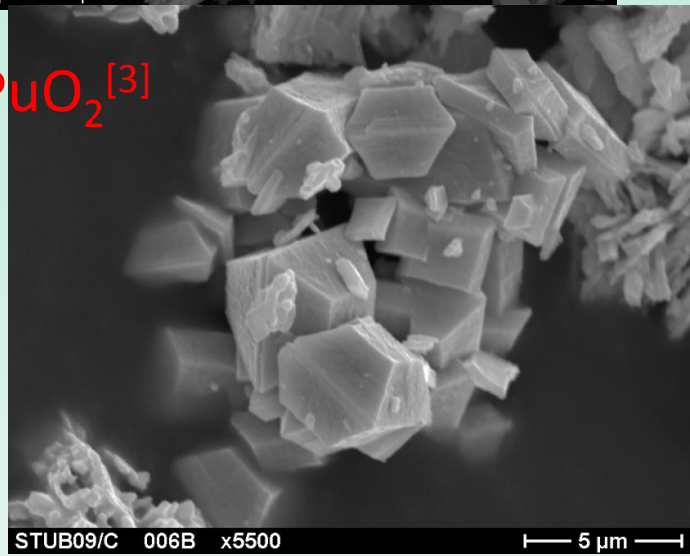
- Impact of surface area is huge.

Scanning Electron Microscopy – Energy Dispersive Spectroscopy





HSSA CeO_2



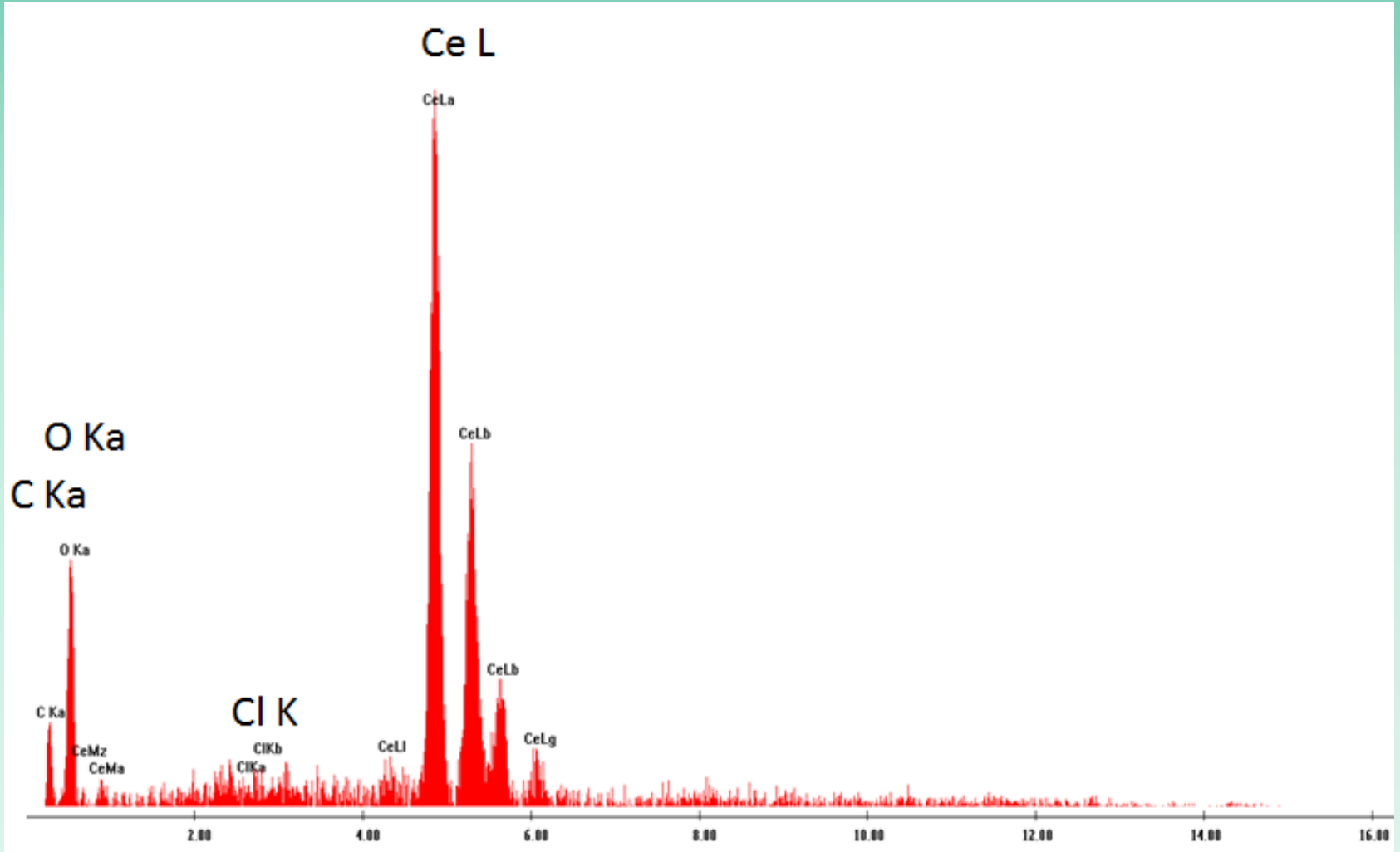
PuO_2[3]

- CeO_2 particles have very different shapes compared to Magnox PuO_2.

3 R. Taylor, *Update on experimental work at NNL underpinning Sellafield plutonium storage*, **2013**

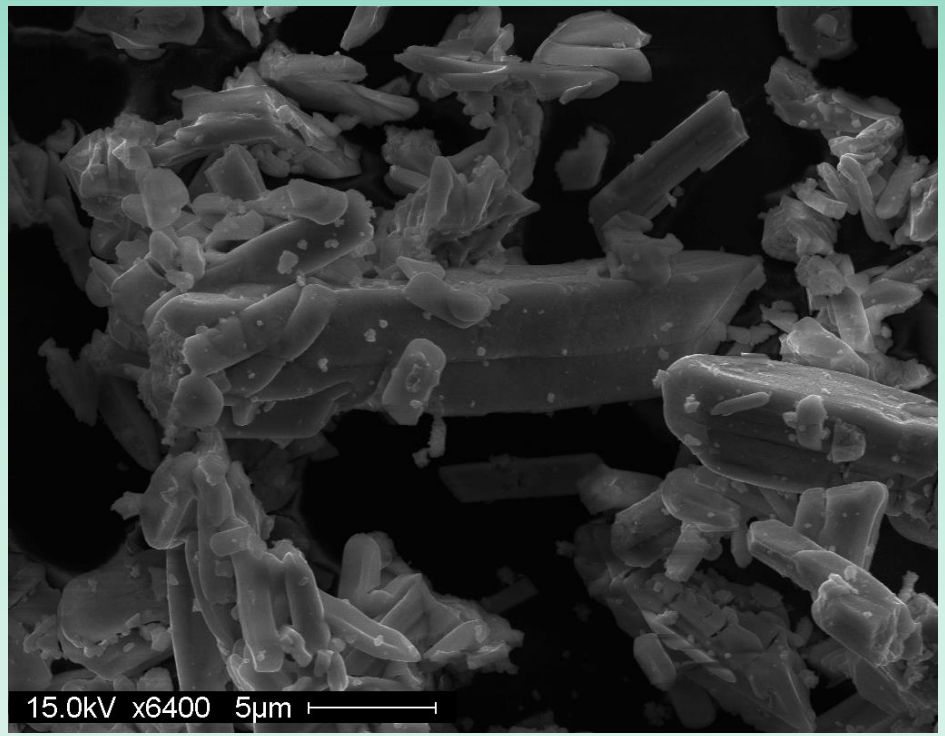
Scanning Electron Microscopy – Energy Dispersive Spectroscopy

Batch 2 HSSA CeO_2

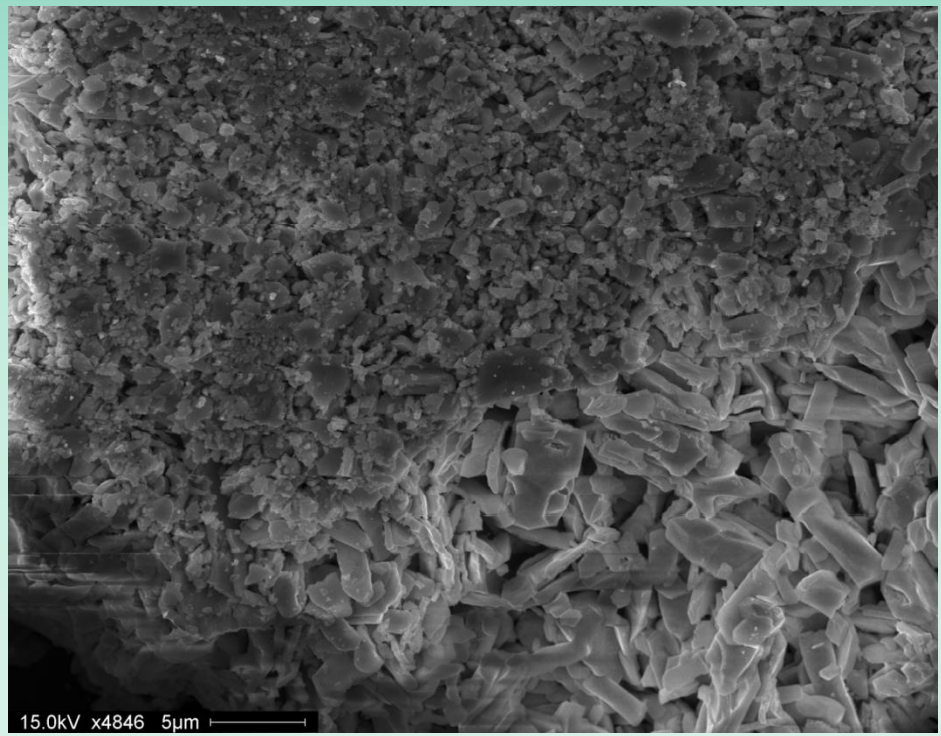


Scanning Electron Microscopy – Energy Dispersive Spectroscopy

LSSA CeO_2



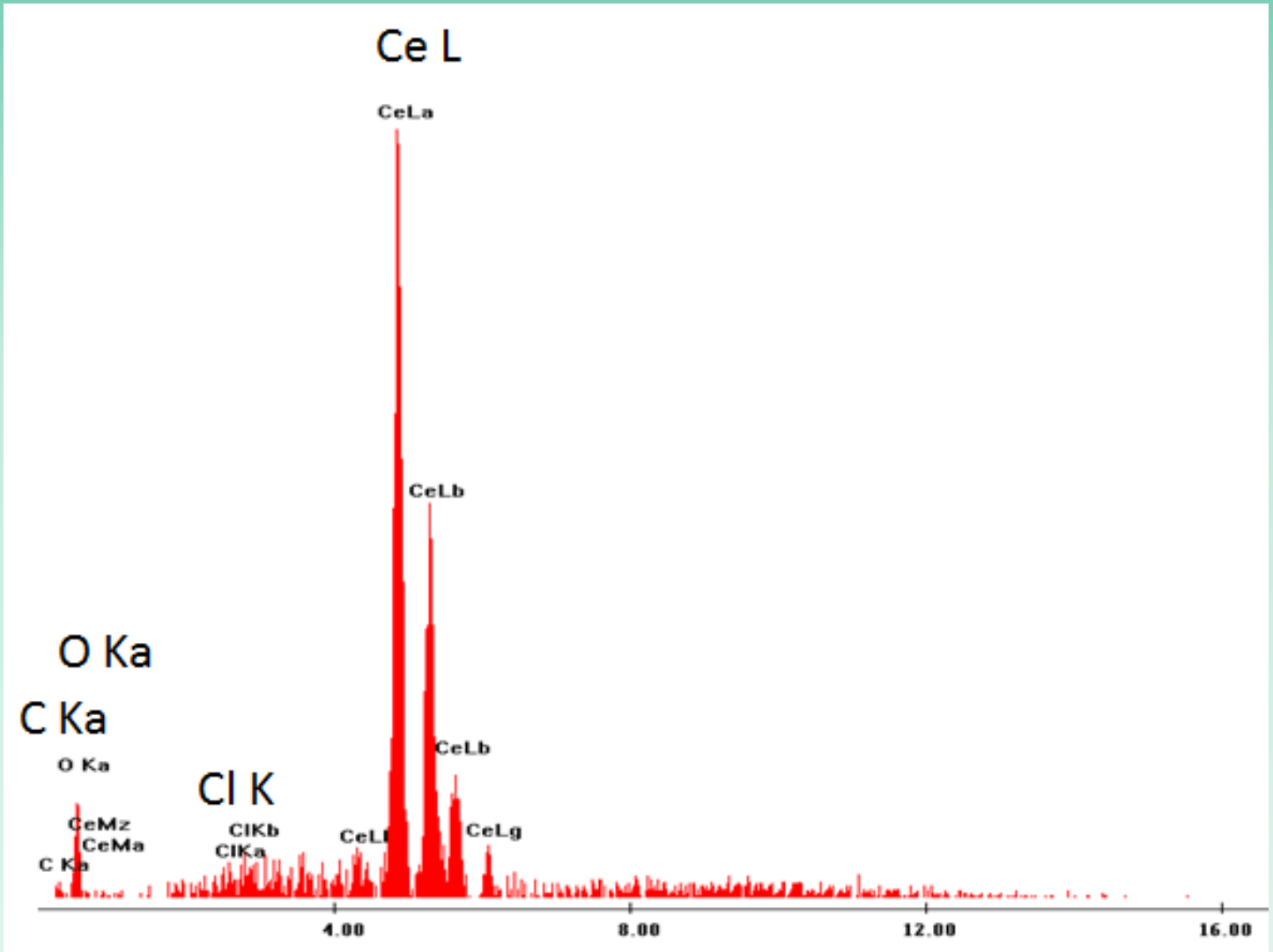
Batch 1



Batch 2

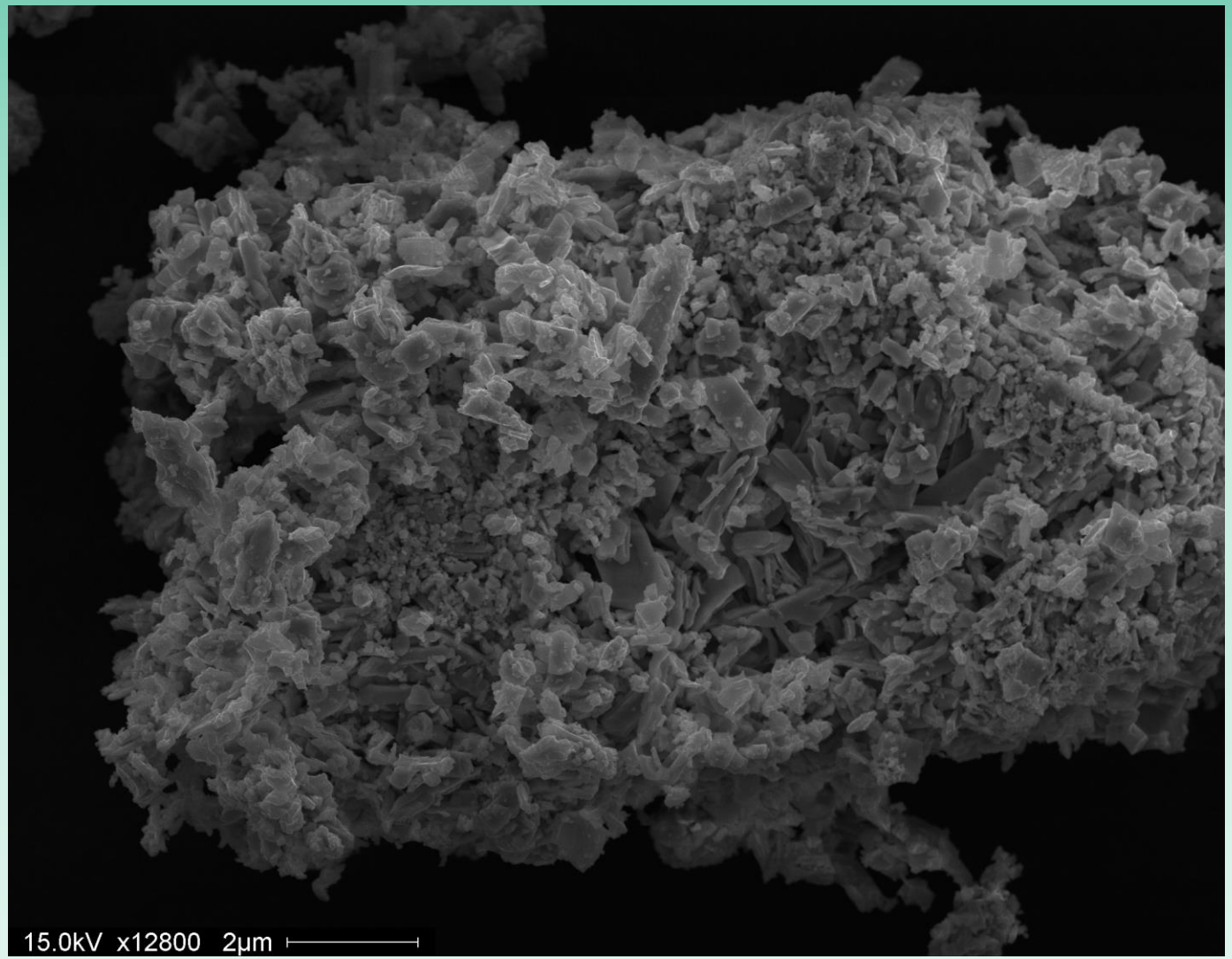
Scanning Electron Microscopy – Energy Dispersive Spectroscopy

Batch 2 LSSA CeO_2



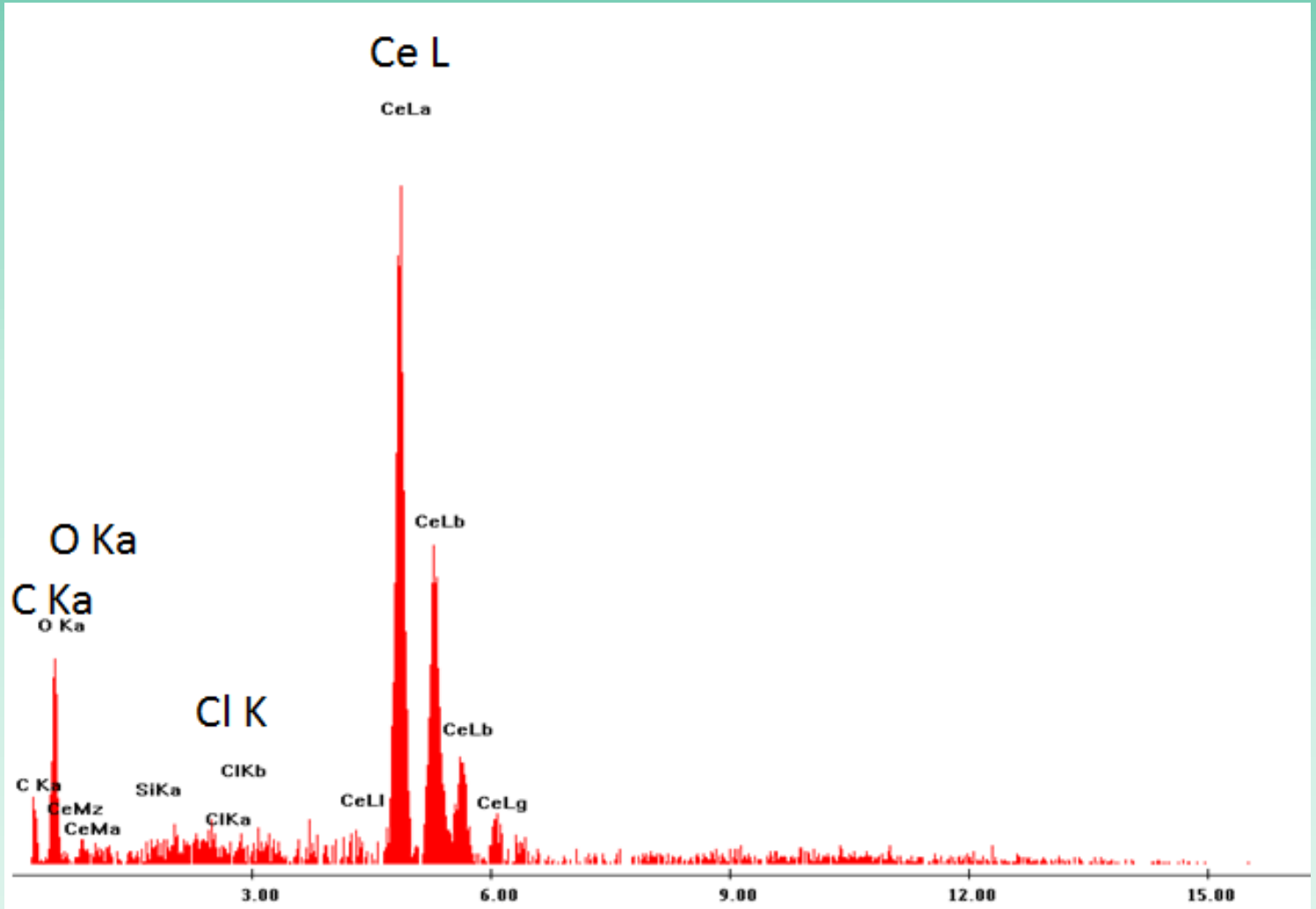
Scanning Electron Microscopy – Energy Dispersive Spectroscopy

Batch 2 LSSA CeO_2 + Cl^-



Scanning Electron Microscopy – Energy Dispersive Spectroscopy

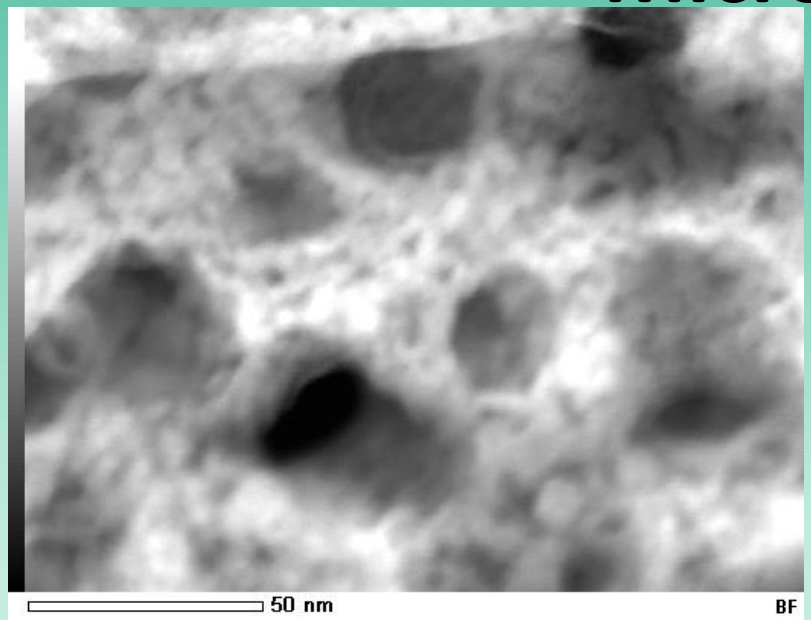
Batch 2 LSSA CeO_2 + Cl^-

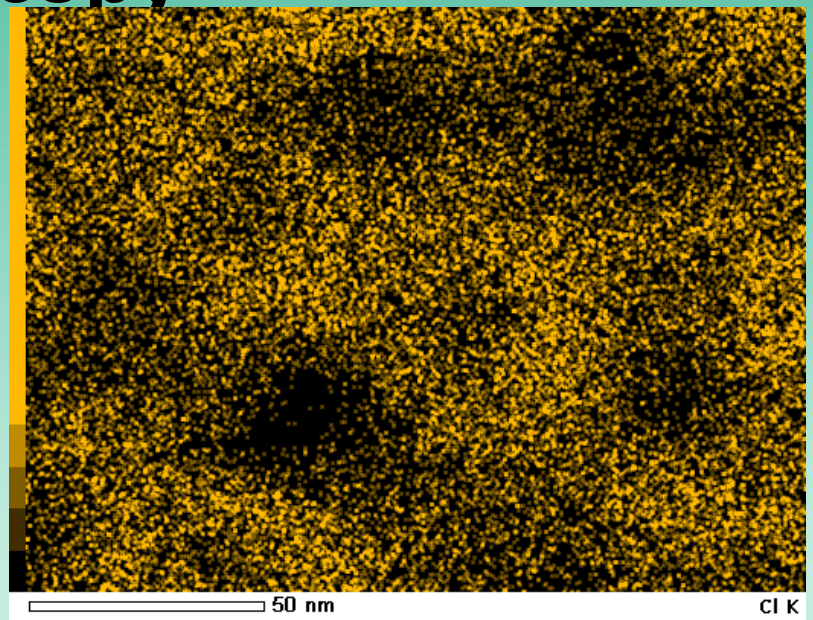


- Not enough Cl^- to detect with EDS.

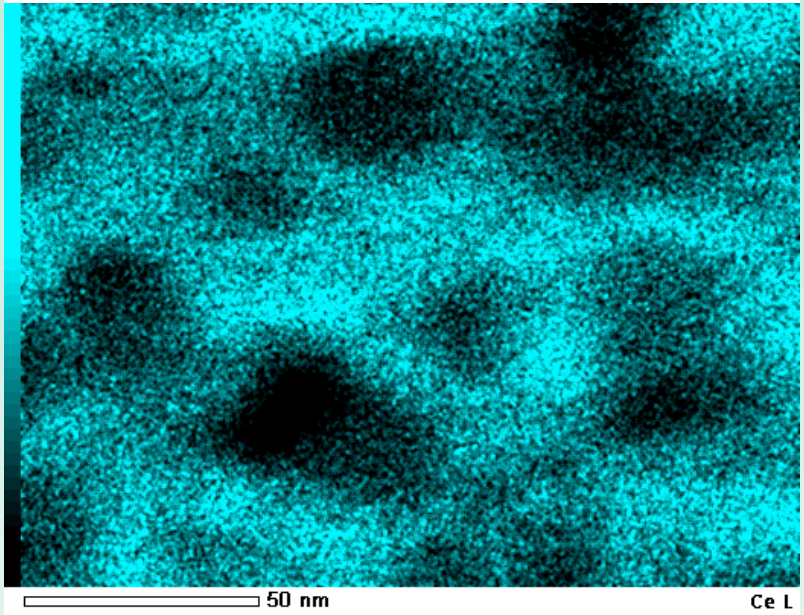
Focussed Ion Beam-Transmission Electron Microscopy

Batch 1 HSSA + Cl^-

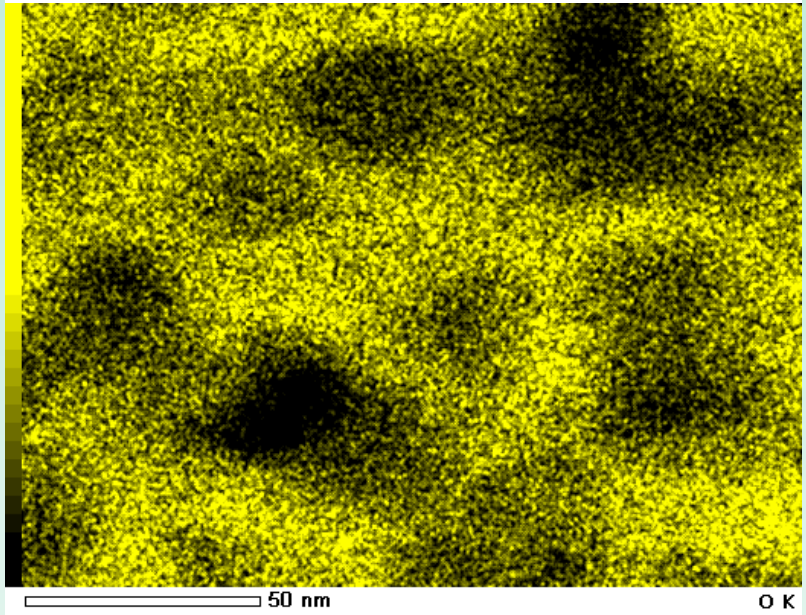




Cl



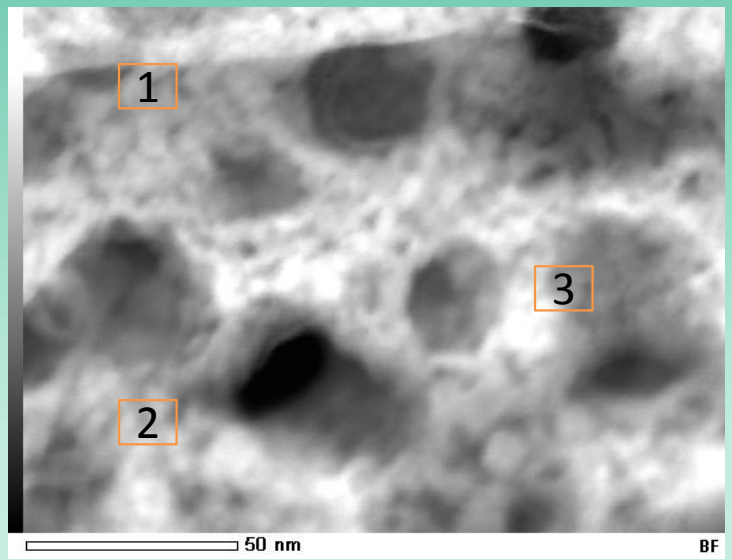
Ce

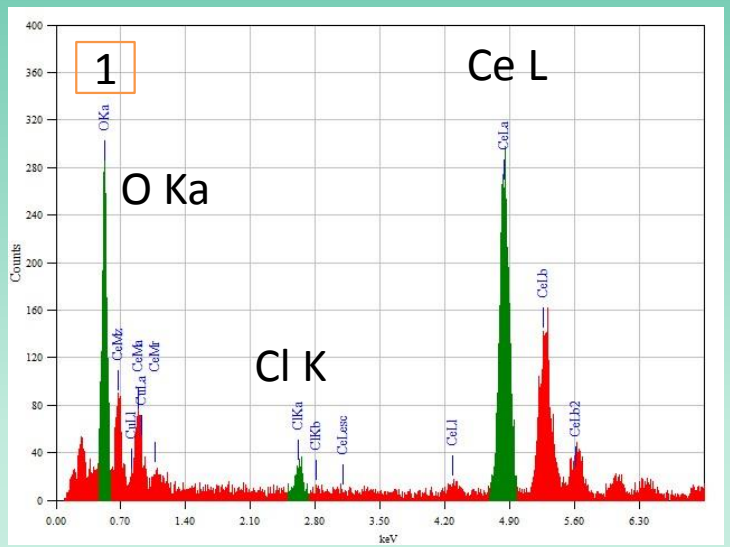


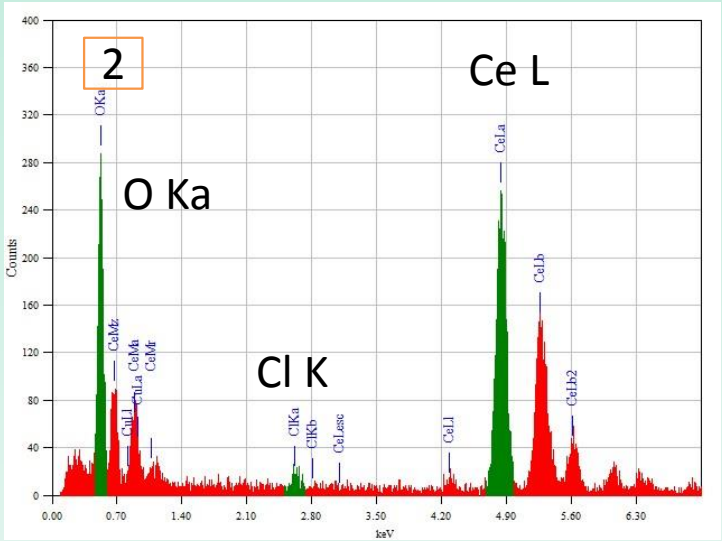
O

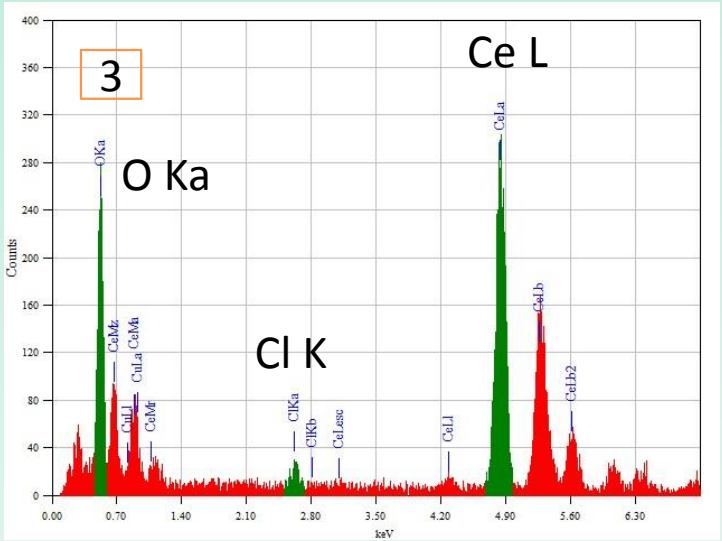
Transmission Electron Microscopy-Energy Dispersive Spectroscopy

Batch 1 HSSA + Cl^-



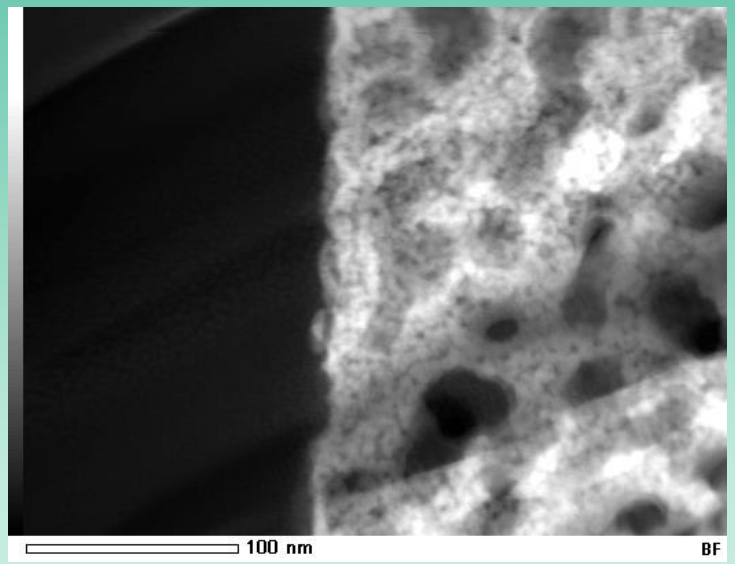


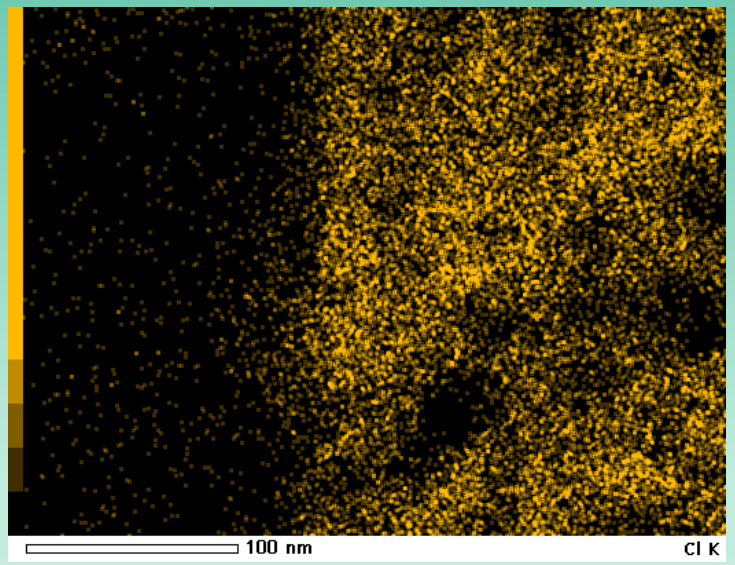




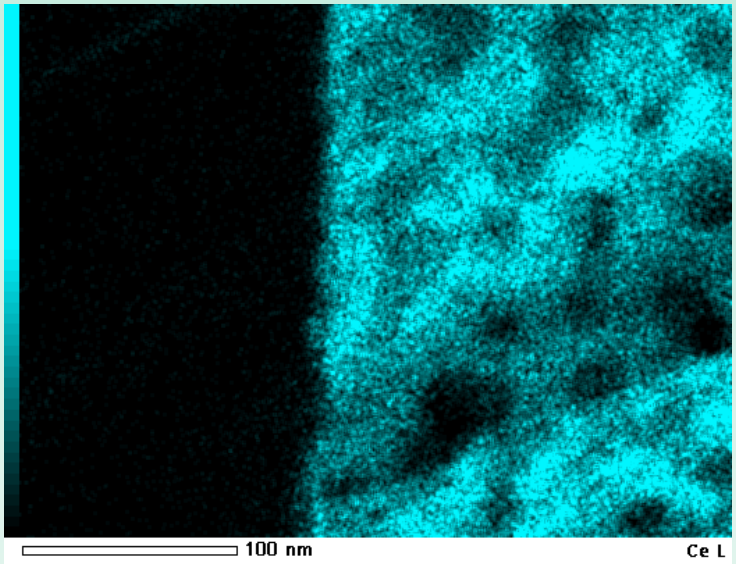
Focussed Ion Beam-Transmission Electron Microscopy

Batch 1 HSSA + Cl^-

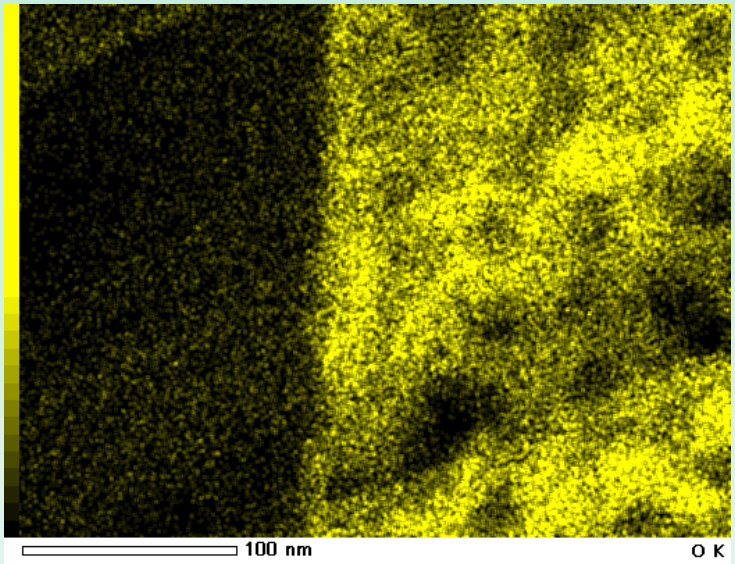




Cl



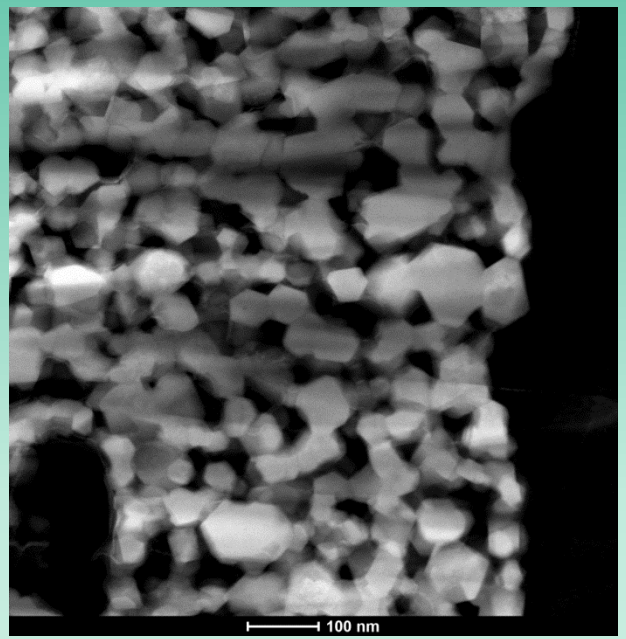
Ce

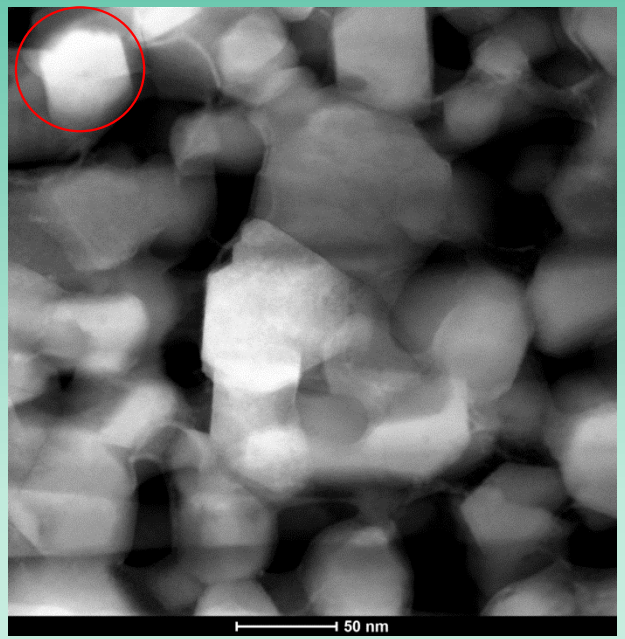


O

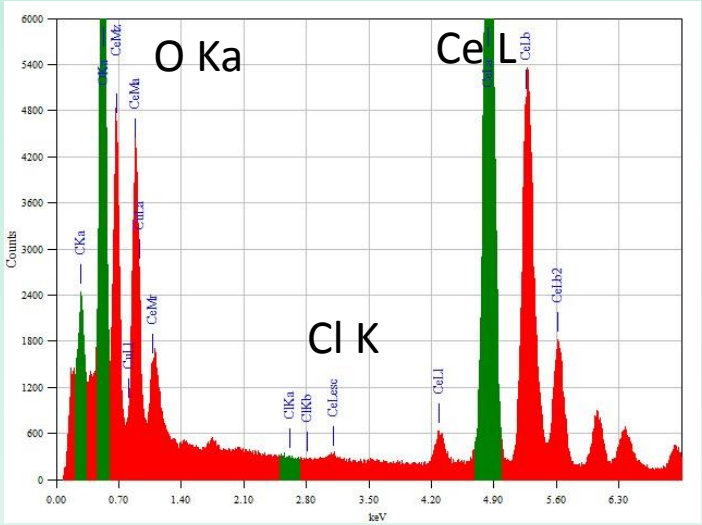
Transmission Electron Microscopy-Energy Dispersive Spectroscopy

100 nm





50 nm



- Cl^--contaminated Batch 1 HSSA CeO_2 heat treated at 900 °C.
- Cl^- is removed to below the limit of detection (1,000 ppm).
- Conditions for acceptance for interim storage are <500 ppm Cl^-.

Conclusions

- Additional phase in Batch 2 HSSA CeO_2 with contamination but not LSSA (XRD).
- IR spectroscopy detects changes in water concentration; XPS detects changes in Cl^- concentration.
- Batch 1 had more Cl^- and water before contamination than after heat treatment at 900 °C (XPS).
- Cl^- is spread homogeneously over the surface and within the pores (elemental mapping).
- Cl^- drops below limit of detection after HSSA heat treatment at 900 °C (EDS).

Future work

- Synthesise more CeO_2 of a range of crystal sizes.
- Contaminate using a range of HCl concentrations and relative humidities.
- Heat treat these over a range of temperatures.
- Carry out leaching experiments – how much Cl^- is in each phase?
- XPS own samples with *in situ* heating and Mass Spectrometry detection of volatilised substances.
- Do the same with ThO_2, synthesised PuO_2 and Magnox PuO_2.
- Carry out experiments at ITU, Germany.

Acknowledgements

- Supervisors.
- Mark Sarsfield (NNL-samples).
- John Waters (UoM-XRD).
- Jon Fellowes (UoM-SEM-EDS).
- Mark Engelhard (PNNL-XPS).
- Bruce Arey (PNNL-SEM-FIB).
- Libor Kovarik (PNNL-TEM-EDS).
- SEM-FIB, TEM-EDS and XPS were done through Rapid Access EMSL User Proposal 48811.
- You for listening!