My Summer ~~Vacation~~

At NCNR!

Exploring the Synthesis and Structure of $Y_{2-x}Ce_xTi_2O_7$ Compounds

Vikas Bhatia

Gaithersburg High School

Overview:

- Motivation
- Background
- Solid State Synthesis of $Y_{2-x}Ce_xTi_2O_7$ Compounds
- Characterization using powder X-ray diffraction
- Experimental Results
- Conclusions
- Future Directions

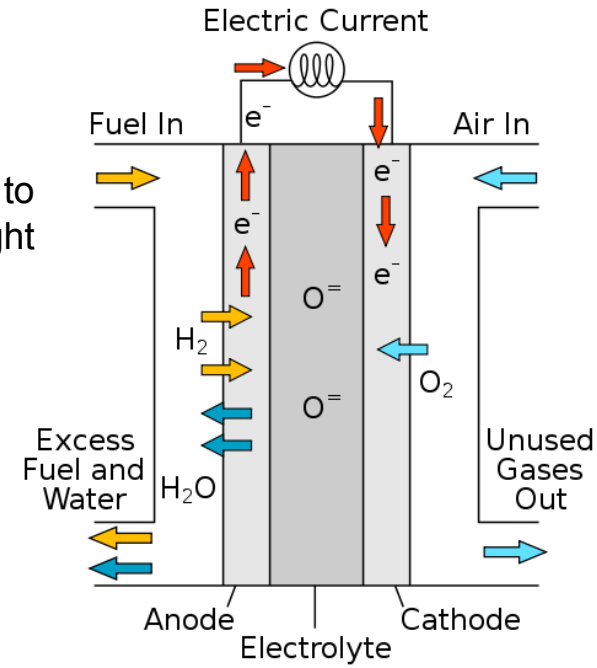
Purpose

- The main goal was to synthesize the $Y_{2-x}Ce_xTi_2O_7$ samples with different concentrations of Ce
- To determine the effect of Ce substitution into structure of the $Y_2Ti_2O_7$ parent compound
- Powder X-ray Diffraction data were measured in order to characterize the samples

Background

CeO_2 is used in automobile catalytic converters and has the ability to release O_2 ($2\ CeO_2 \leftrightarrow Ce_2O_3 + ½\ O_2$). This ability to release O_2 might suggest applications of CeO_2 as a water oxidation catalyst.

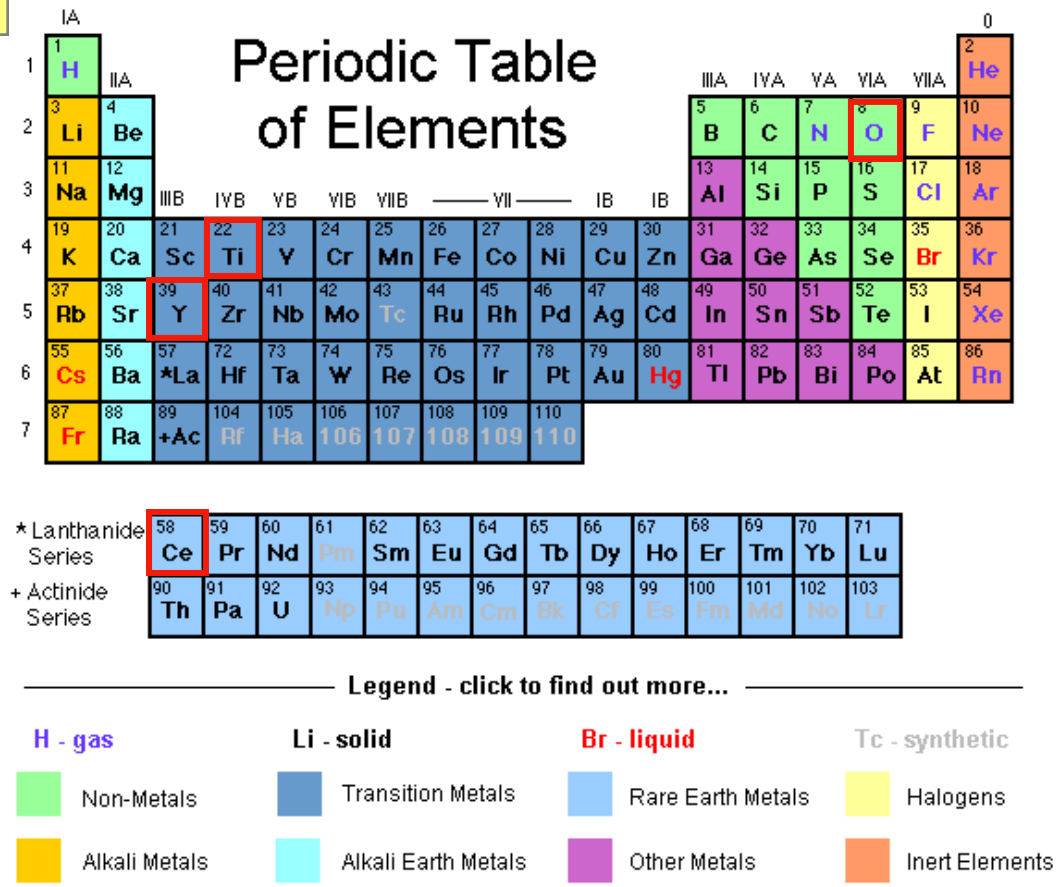
[hydrocarbons] + $O_2 \rightarrow CO_2 + H_2O$

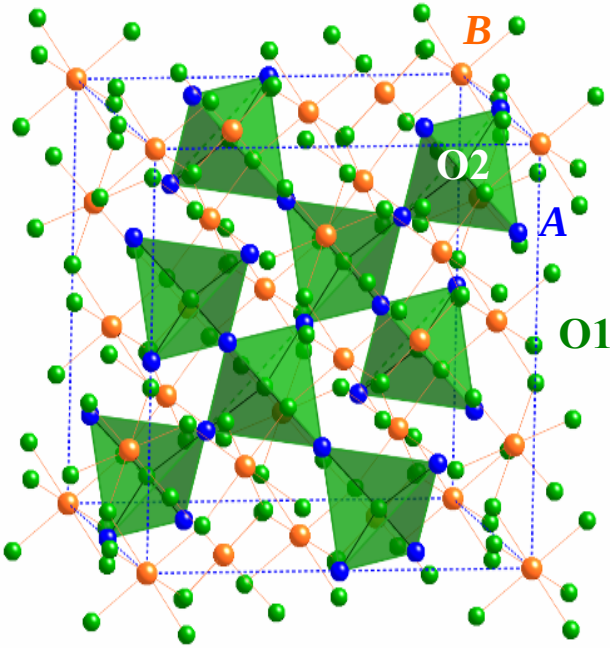


http://en.wikipedia.org/wiki/Solid_oxide_fuel_cell

$Y_2Zr_2O_7$ has been studied as a possible alternative solid oxide electrolyte

Kumar, M.; Raj, I. A.; Pattabiraman, R.; Mater. Chem. Phys. 108 (2008) pp. 102-108.





$A = Y^{+3}$

$B = Ti^{+4}$

cubic ($Fd3$-m)

$a = 9.74$ Å

The structure of $A_2B_2O_7$. The O_2 atoms are omitted for clarity.

The structure of the oxide pyrochlore (shown above) can be denoted as $A_2B_2O_7$, where the A^{+3} site is occupied by a trivalent cation and the B^{+4} site is occupied by a transition metal.

Becker, W.J.;Will, G., Zeitschrift fuer Naturforschung, Teil B. Anorganische Chemie, Organische Chemie **24,** 1969, pp. 259-259

Experimental

- Calculate the amounts of TiO_2, Y_2O_3, and CeO_2 to be weighed out to synthesize the different concentrations of Ce into $Y_{2-x}Ce_xTi_2O_7$ (x = 0, 0.05, 0.15, 0.25, 0.5, 0.8, 1, 1.25).

$$2\ TiO_2 + x\ CeO_2 + \left(\frac{2-x}{2}\right) Y_2O_3 \rightarrow Y_{2-x}Ce_xTi_2O_7$$

Microsoft Excel - Book1(1).xls

File Edit View Insert Format Tools Data Window Help

Go to Office Live | Open | Save

D10 =((B7*C10*225.79)/((88.906*(2-A10))+(140.12*A10)+(95.734)+(15.999*7)))

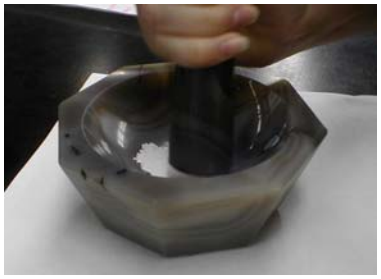
	A	B	C	D	E	F
1	Molecular Weights					
2	Cerium	140.12				
3	Yitrium	88.906				
4	Oxygen	15.999				
5	Titanium	47.867				
6						
7	sample size(g)	12				
8						
9	composition of cerium	grams of titanium	moles of yitrium oxide	grams of yitrium oxide	moles of cerium oxide	grams of cerium oxide
10	1.25	4.26313489	0.375	2.260127481	1.25	5.742459513
11						

Starting Materials for Samples Synthesized

Concentration of Cerium	Final Product (g)	TiO_2 (g)	Y_2O_3 (g)	CeO_2 (g)
x = 0	7	2.907	4.1032	0
x = 0.05	12	3.9385	6.8072	0.2664
x = 0.15	12	4.8729	6.3739	0.7883
x = 0.25	12	4.6624	4.9435	2.5120
x = 0.5	12	4.4945	3.8128	3.8740
x = .8	12	4.4939	3.8113	3.8742
x = 1	12	4.3878	3.1022	4.7283
x = 1.25	12	4.2640	2.2610	5.7428
x = 2	12	3.9280	0	8.4659

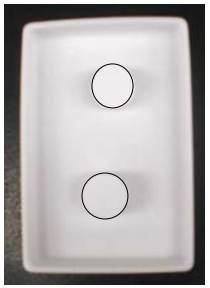
Solid State Reaction or “Shake and Bake” Method

Step 1



Mix the solution
For every 15 minutes grinding = 1 day of heat
Increases surface reactivity

Step 2



Aids in reactivity and homogeneity of the sample

Step 3

- Provides activation energy for product formation
- Helps mix the reactants
- Aids in sintering pellets

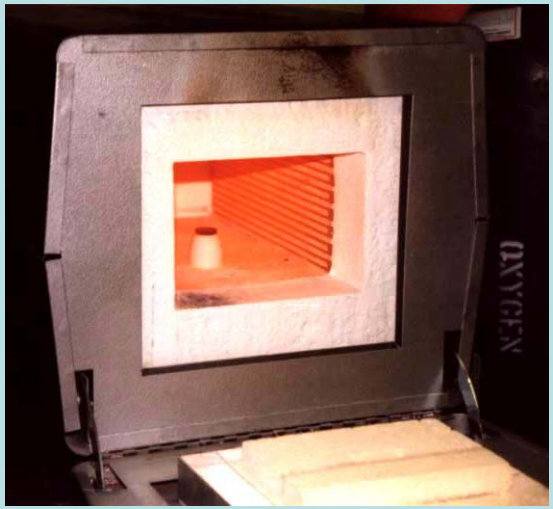
High Temperature Experimental Considerations

- Crucible & Reaction Cell
- Furnace
- Reaction Temperature
- Starting Materials
- Atmosphere
- Growth Conditions
- Product Form

The samples were synthesized using Solid State Reaction

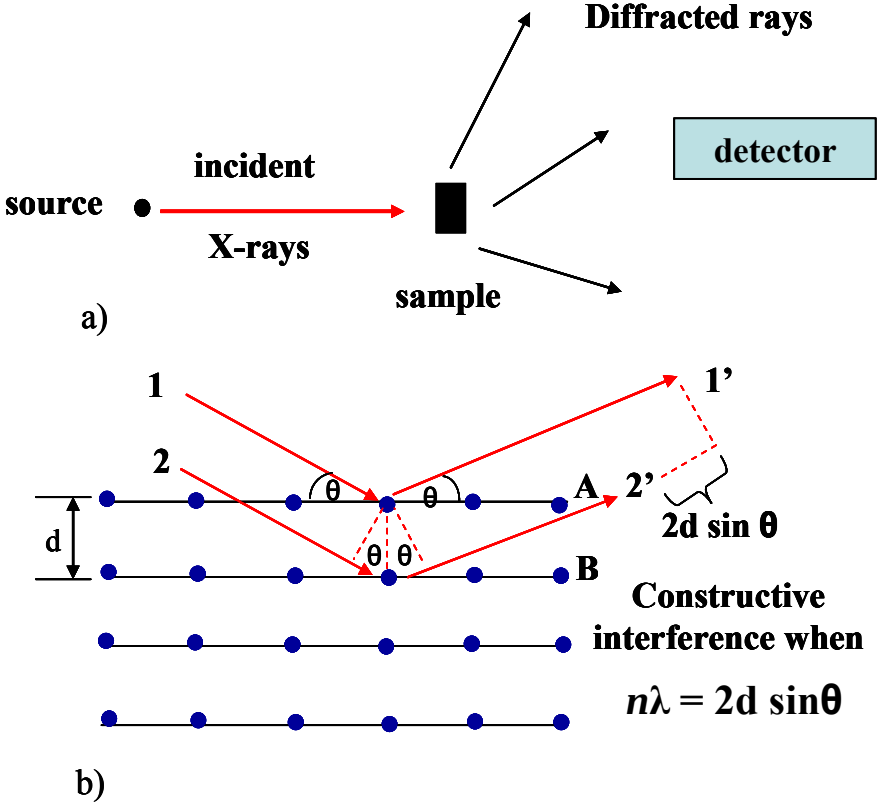
Steps in Conventional Solid State Reaction

1. Select appropriate starting materials
2. Weigh out starting materials
3. Mix starting materials together using mortar and pestle
4. Overnight Heat at 1173 K
5. Samples Cooled to Room Temperature (298 K)
6. Samples were re-mixed
7. Samples were Pressed into pellets using a laboratory press
8. Samples were heated to 1523 K – 1673 K
9. Grind product and analyze (x-ray powder diffraction)
10. If reaction incomplete repeat steps 6-8.



X-ray Powder Diffraction was used to determine if the sample was in the correct phase

Bragg's Law: $n\lambda = 2d \sin \theta$

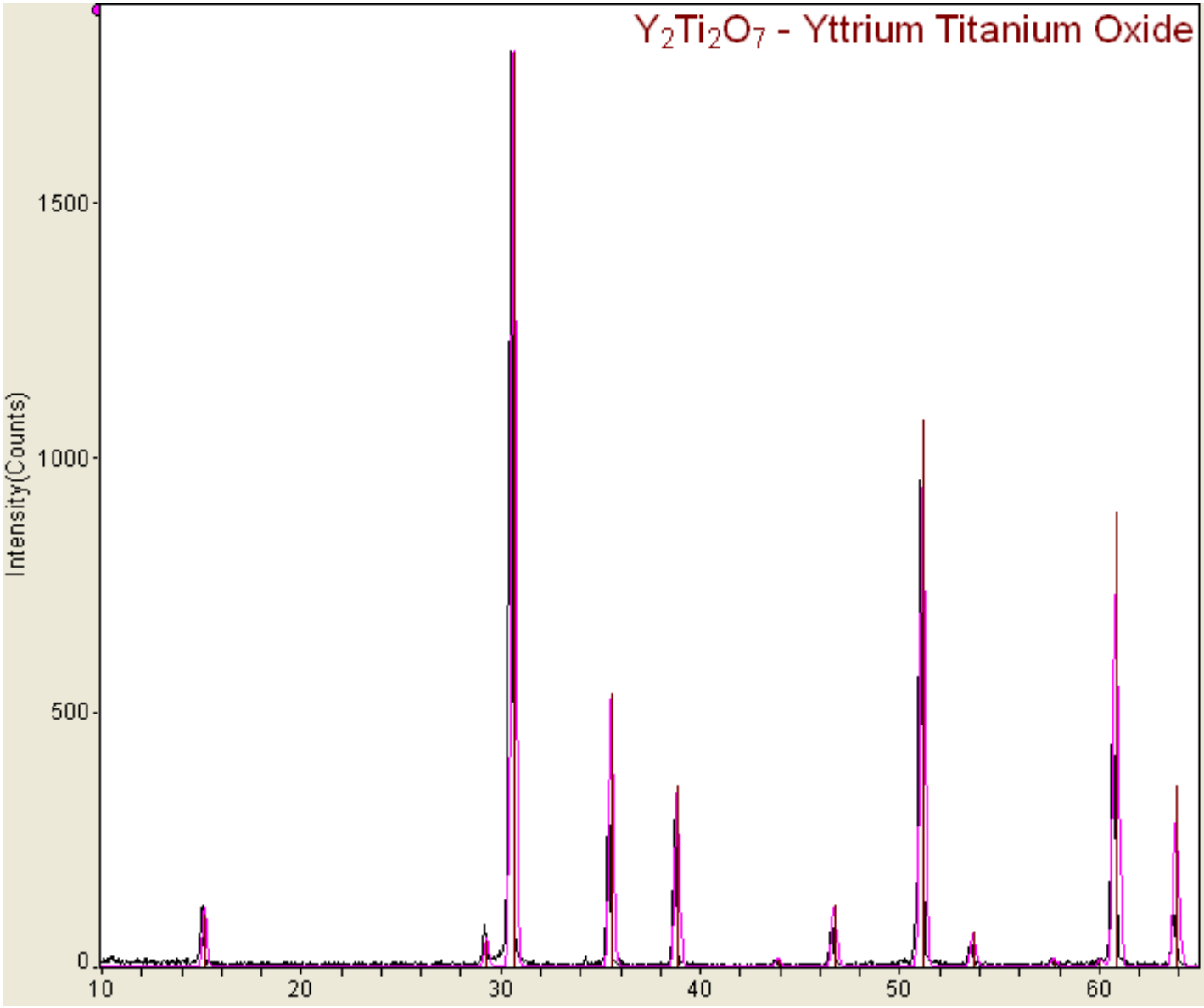


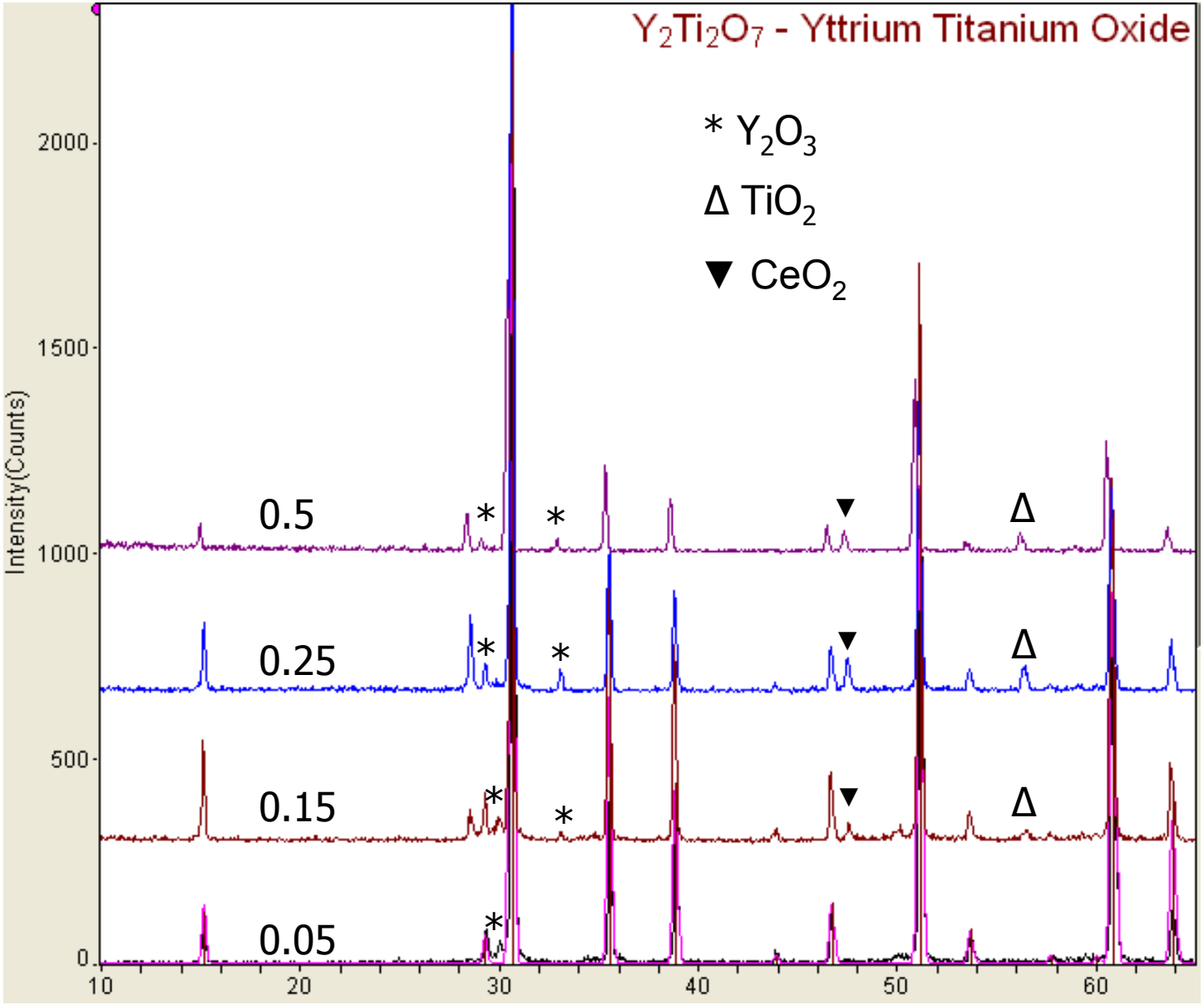
Primary tool for phase analysis in solid state materials

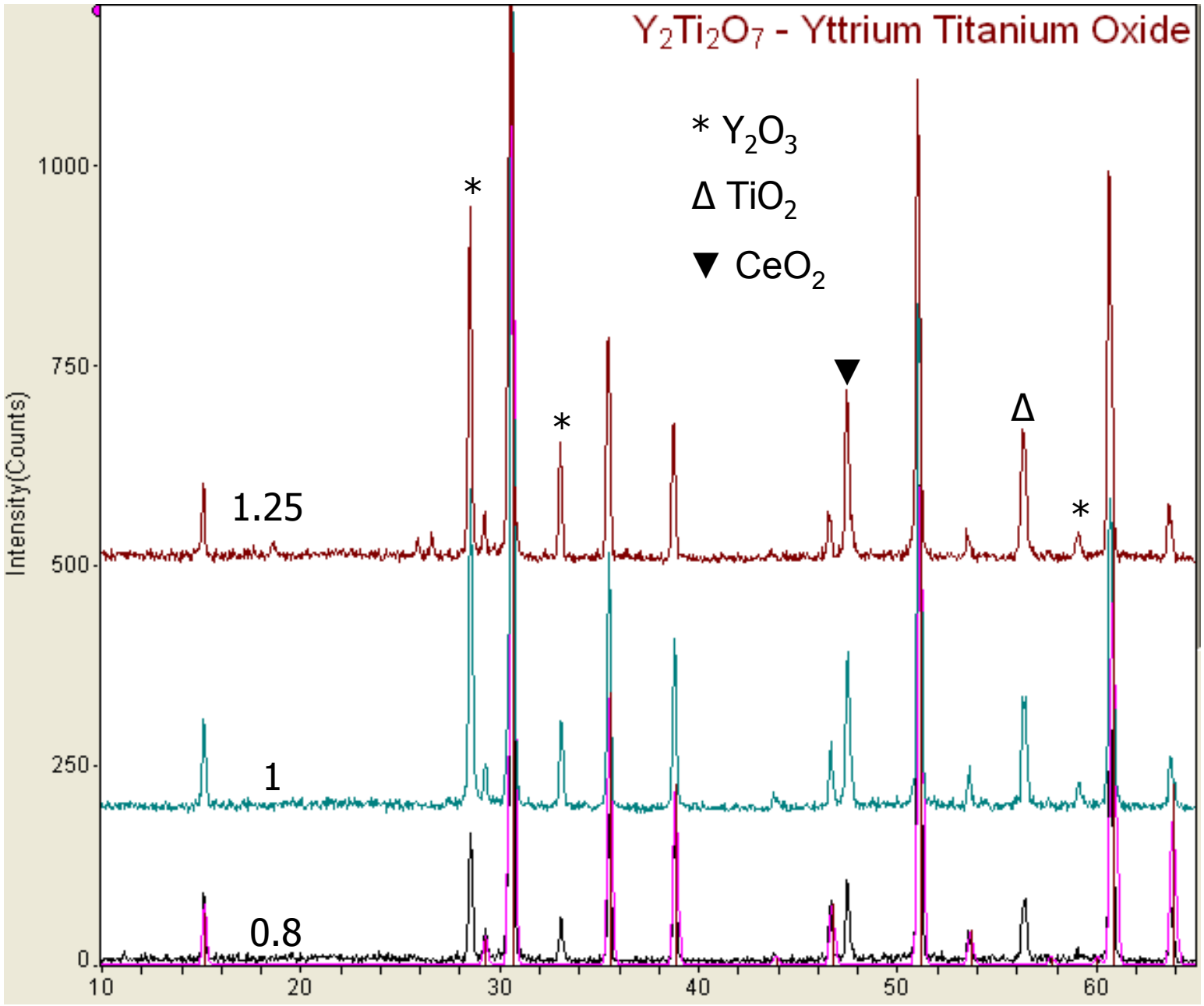
Adapted from: West, A. R., *Basic Solid State Chemistry*. 2nd ed.; John Wiley & Sons: New York, 1999, pp. 134-135.

n = an integer determined by the order given
λ = the wavelength of X-rays
d = perpendicular spacing between the two planes in the atomic lattice
θ = angle between the incident ray and the scattering planes

X-ray Powder Diffraction Results




$Y_2Ti_2O_7$ - Yttrium Titanium Oxide
* Y_2O_3
Δ TiO_2
▼ CeO_2
Intensity(Counts)
2000
1500
1000
500
0
10
20
30
40
50
60
0.5
0.25
0.15
0.05


$Y_2Ti_2O_7$ - Yttrium Titanium Oxide
* Y_2O_3
Δ TiO_2
▼ CeO_2
Intensity(Counts)
1000
750
500
250
0
10
20
30
40
50
60
1.25
1
0.8
*
*
▼
Δ
*

Conclusions

- The x = 0, 0.05, 0.15, 0.25, and 0.5 samples adopted the cubic $Y_2Ti_2O_7$ parent structure type.
- In the impurities which were due to TiO_2 and Y_2O_3
- The x = 0.8, 1, 1.25, and 2 needed additional heat and grinds to reach the right phase

Concentration of Cerium	Heat Treatments	PXRD Majority Phase	Impurities
x = 0	1	Cubic	None
x = 0.05	1	Cubic	Very small amount of Y2O3
x = 0.15	3	Cubic	Very small amounts of Y203, TiO2, and CeO2
x = 0.25	3	Cubic	Very small amounts of Y2O3, TiO2, and CeO2
x = 0.5	3	Cubic	Small amounts of Y2O3, TiO2, and CeO2
x = .8	2	Cubic with many impurities	Large amounts of Y2O3, TiO2, CeO2
x = 1	1	Cubic with many impurities	Large amounts of Y2O3, TiO2, CeO2
x = 1.25	1	Cubic with many impurities	Very large amounts of Y2O3, TiO2, CeO2
x = 2	1	Unknown	Unknown

Future Experiments

Next Step: Neutron Powder Diffraction Experiments

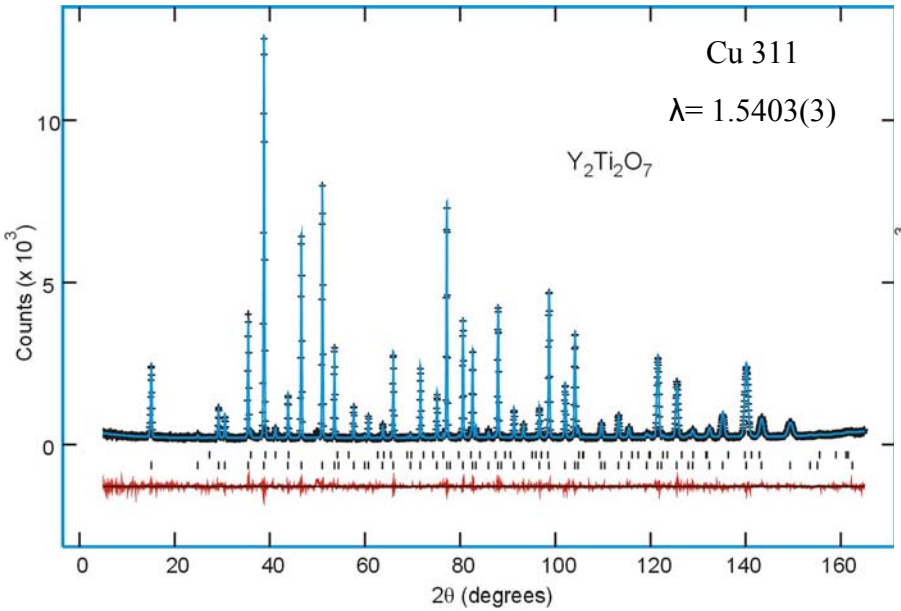
There are several bits of information that we would like to know about the above samples:

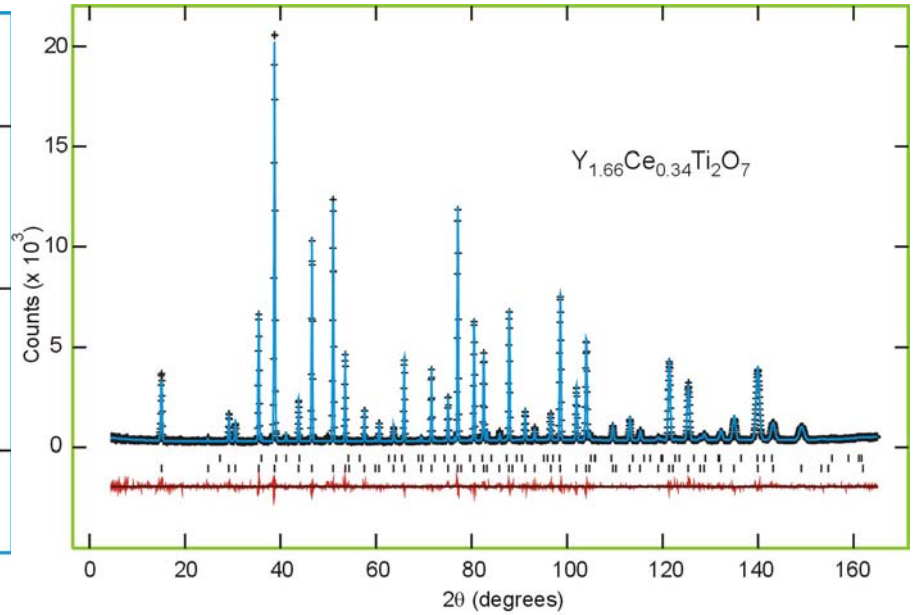
- Are there any oxygen deficiencies? Oxygen deficiencies will affect the electrocatalytic ability of the compound.

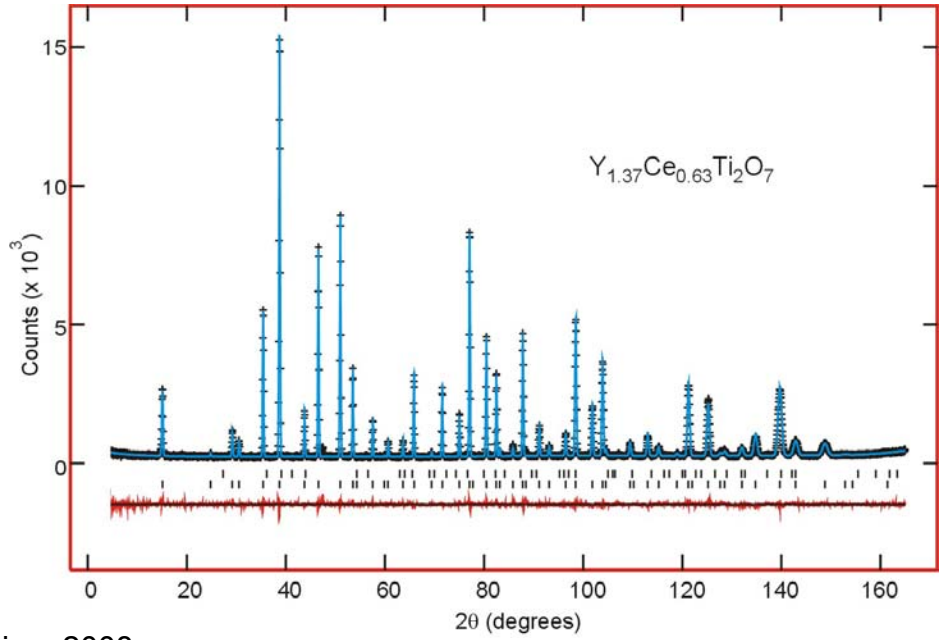
- Is there a specific site that the Ce atoms prefer to occupy? This may be important in fully understanding the resulting electrocatalytic reactivity.

- What is the effect of Ce substitution on bond distances throughout the structure? This will aid in understanding the structural constraints of the addition of Ce into this cubic structure.

Previous Neutron Powder Diffraction Experiments on BT1



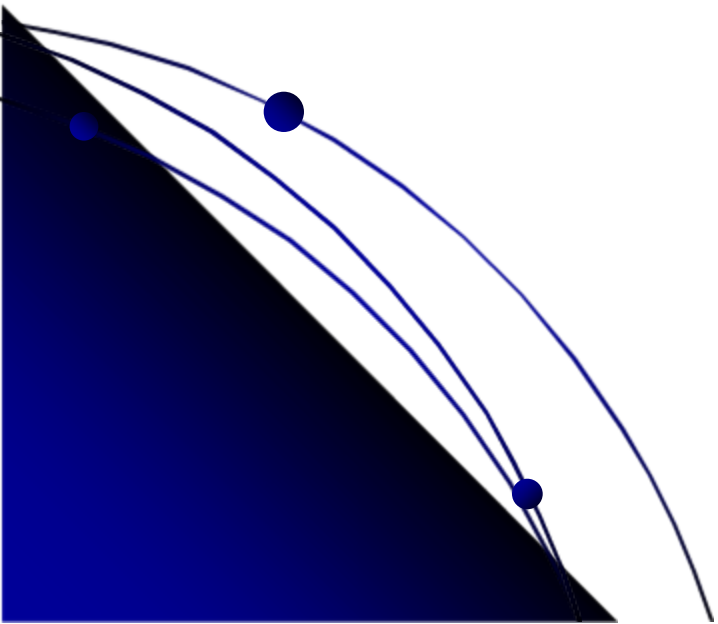




Millican, J. N.; et al., In preparation, 2008.

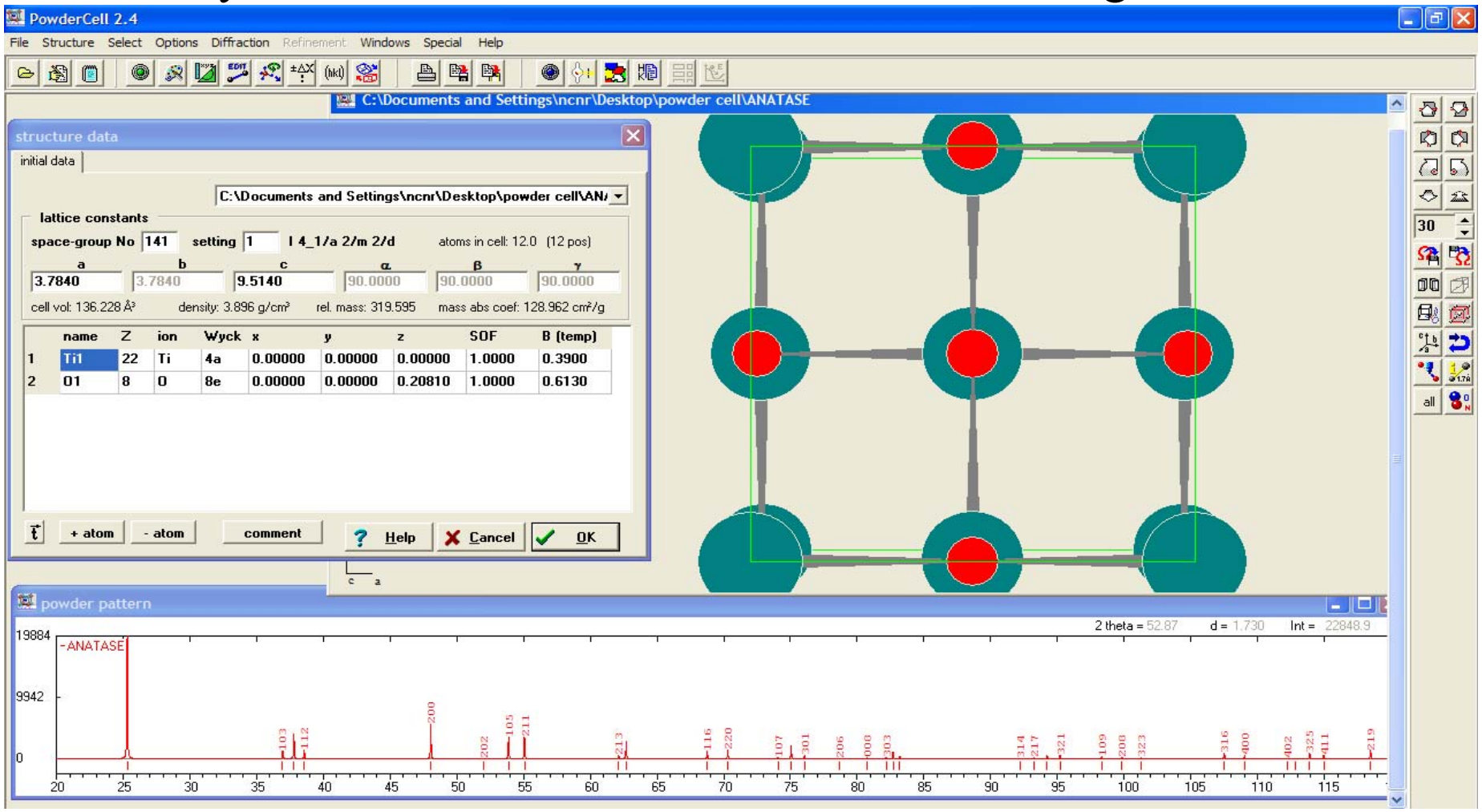
Accomplishments

- $Y_{2-x}Ce_xTi_2O_7$ Experiment
- Powder Cell Program
- Balls and Sticks
- EXPGUI



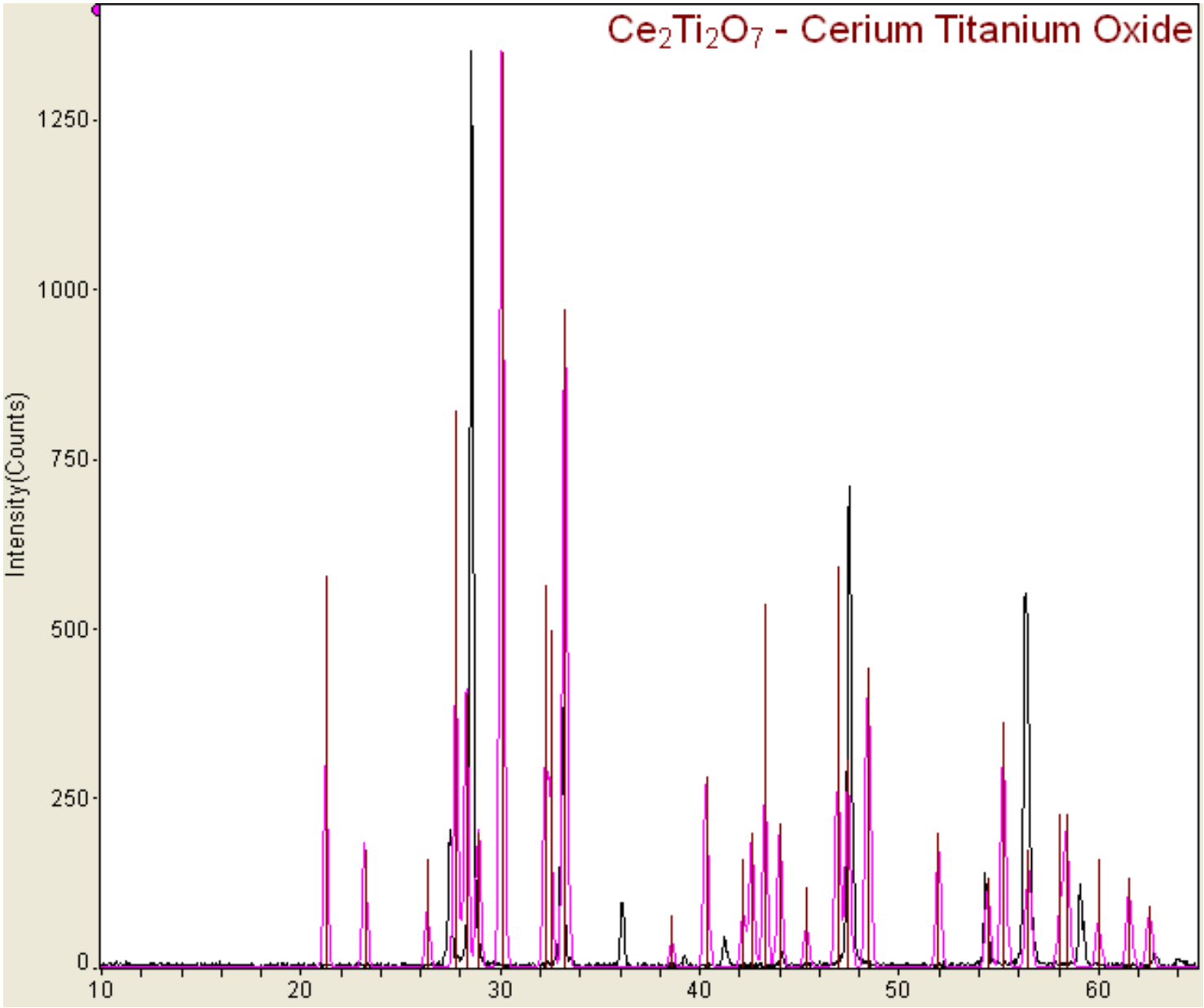
Powder Cell

- X-ray and Neutron Powder Diffraction modeling



Acknowledgements

- Dr. Jasmine Millican, Mentor
- NIST/NCNR
- Dr. Robert Dimeo
- Dr. Dan Neumann
- Yamali Hernandez
- Kim Tomasi
- Dr. Daniel Phelan
- Dr. Larry Kneller
- Dr. Judith Stalick


$Ce_2Ti_2O_7$ - Cerium Titanium Oxide
Intensity(Counts)
1250
1000
750
500
250
0
10
20
30
40
50
60