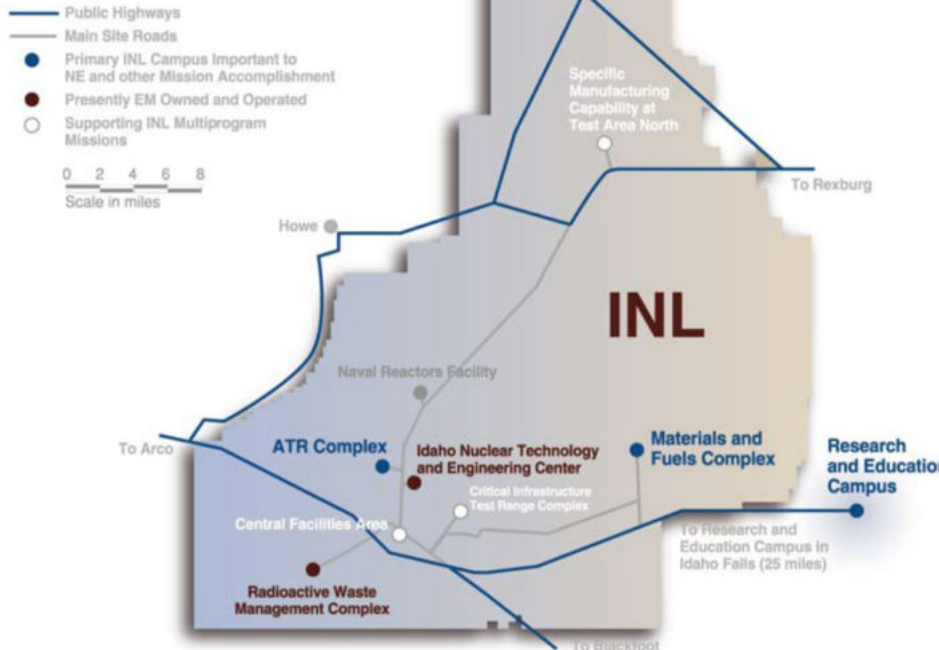


Insight into Solid Oxide Proton Conductors with Dopants by Use of PAS

Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415 US

J. Urban-Klaehn, C.Y. Regalado Vera, W.F. Bauer, Hanping Ding, Dong Ding

309,133 ACRES
889 Square Miles

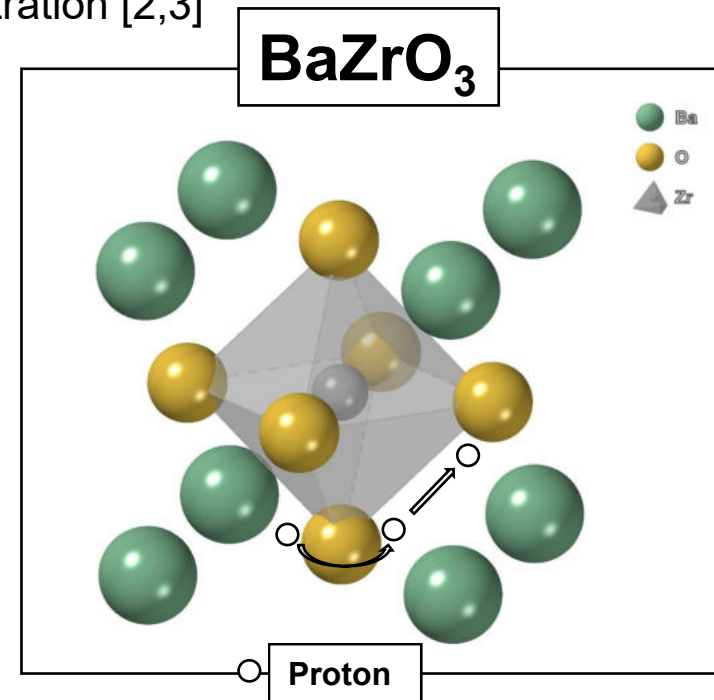


Proton conducting solid oxides

- Proton conducting solid oxides have found application in fuel cells, electrolytes, hydrogen sensors and membrane reactors [1]
- Doped BaZrO₃ (BZO) is a material that shows promising proton conduction that depends on the doping elemental and doping concentration [2,3]
- Doping of Zr site by a trivalent element creates oxygen vacancies V_O^{••}
- Protons are incorporated by the hydration of V_O^{••}:



- Protons are bonded to oxygen and diffuse in the material by jumping from oxygen to oxygen



[1] Iwahara H, Asakura Y, Katahira K, Tanaka M. Prospect of hydrogen technology using proton-conducting ceramics. Solid State Ionics. 2004;168(3-4):299-310.

[2] Kreuer KD, Adams S, Munch W, Fuchs A, Klock U, Maier J. Proton conducting alkaline earth zirconates and titanates for high drain electrochemical applications. Solid State Ionics. 2001;145:295-306.

[3] Han D, Shinoda K, Sato S, Majima M, Uda T. Correlation between electroconductive and structural properties of proton conductive acceptor-doped barium zirconate. Journal of Materials Chemistry A. 2015;3(3):1243-50.

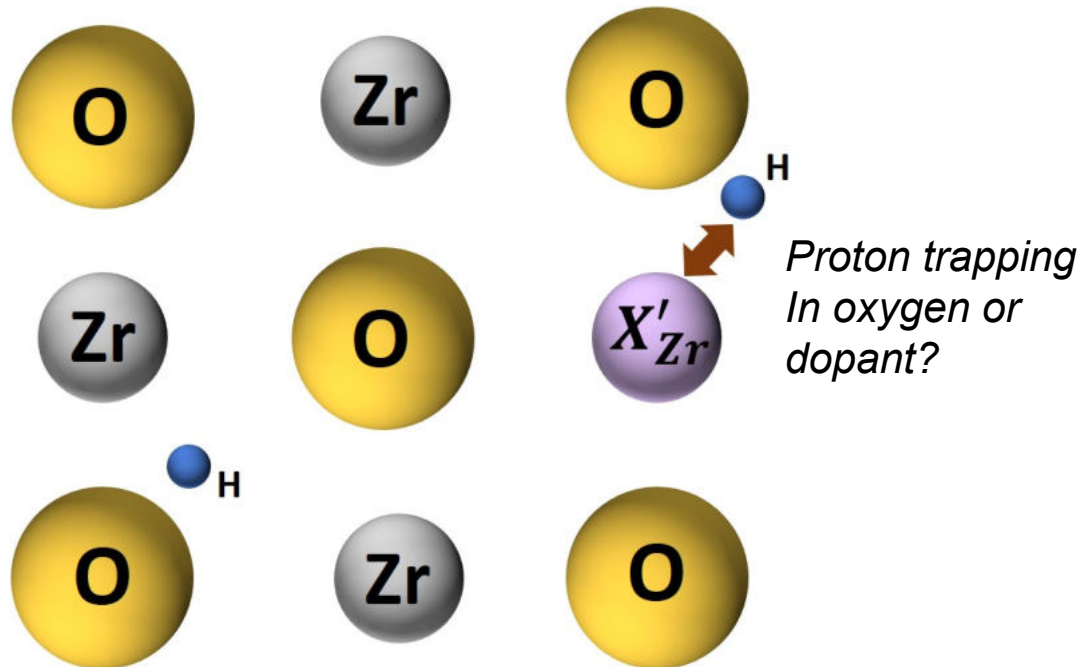
Proton conduction affected by dopant atoms

- Dopants stabilize metal oxide structure but they also contribute to some problems
- Protons can be attracted to dopant atoms due their negative charge; this association causes proton trapping and reduces the proton conductivity [1]

- Important to characterize proton trapping as function of:

- Dopant element
- Doping concentration

- Necessary to probe proton localization in material (i.e., NMR [1,2])



[1] Yamazaki Y, Blanc F, Okuyama Y, Buannic L, Lucio-Vega JC, Grey CP, et al. Proton trapping in yttrium-doped barium zirconate. *Nature Materials*. 2013;12(7):647-51.

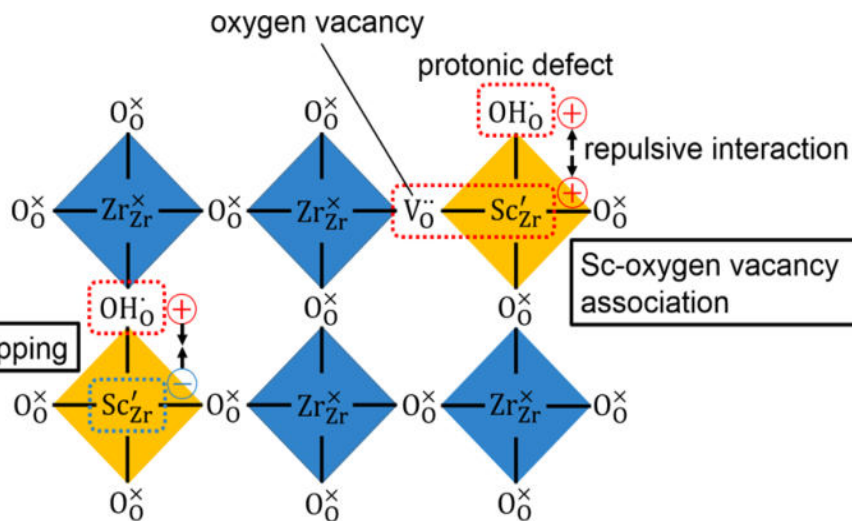
[2] Oikawa I, Takamura H. Correlation among Oxygen Vacancies, Protonic Defects, and the Acceptor Dopant in Sc-Doped BaZrO₃ Studied by ⁴⁵Sc Nuclear Magnetic Resonance. *Chemistry of Materials*. 2015;27(19):6660-7.

Complicated metal/oxygen complexes are created; sometimes depending on the concentration of the dopant

➤ How does the proton concentration affect the proton trapping?

Electron density modified by protons:

- $Zr - O - Zr$ (negative)
- $Zr - OH_O - Zr$ (+)
- $Sc' - OH_O - Zr$ (neutral)
- $Sc' - OH_O - Sc'$ (negative)

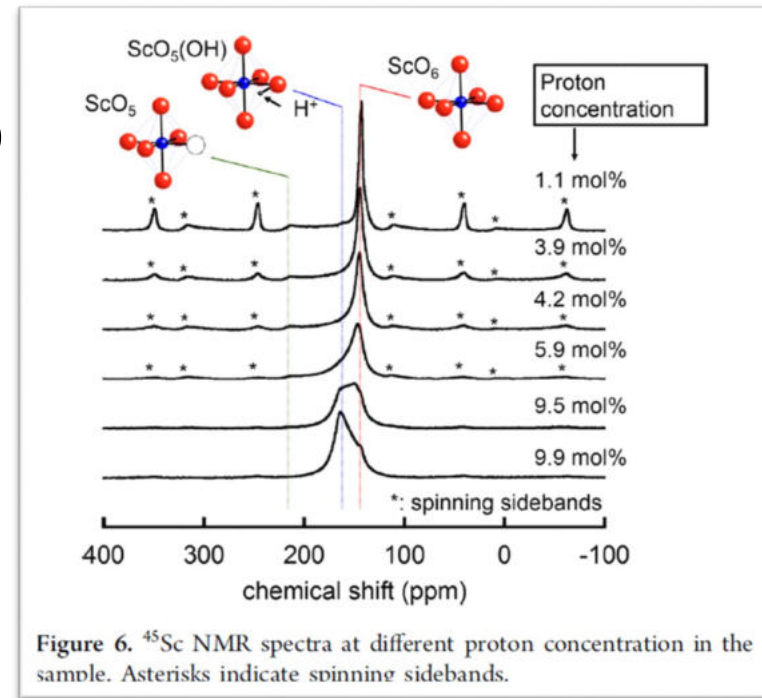


(Figure from *Chem. Mater.* 2015, 27, 6660–6667)

○ Proton concentration:

$$\frac{T_2}{I_2}$$

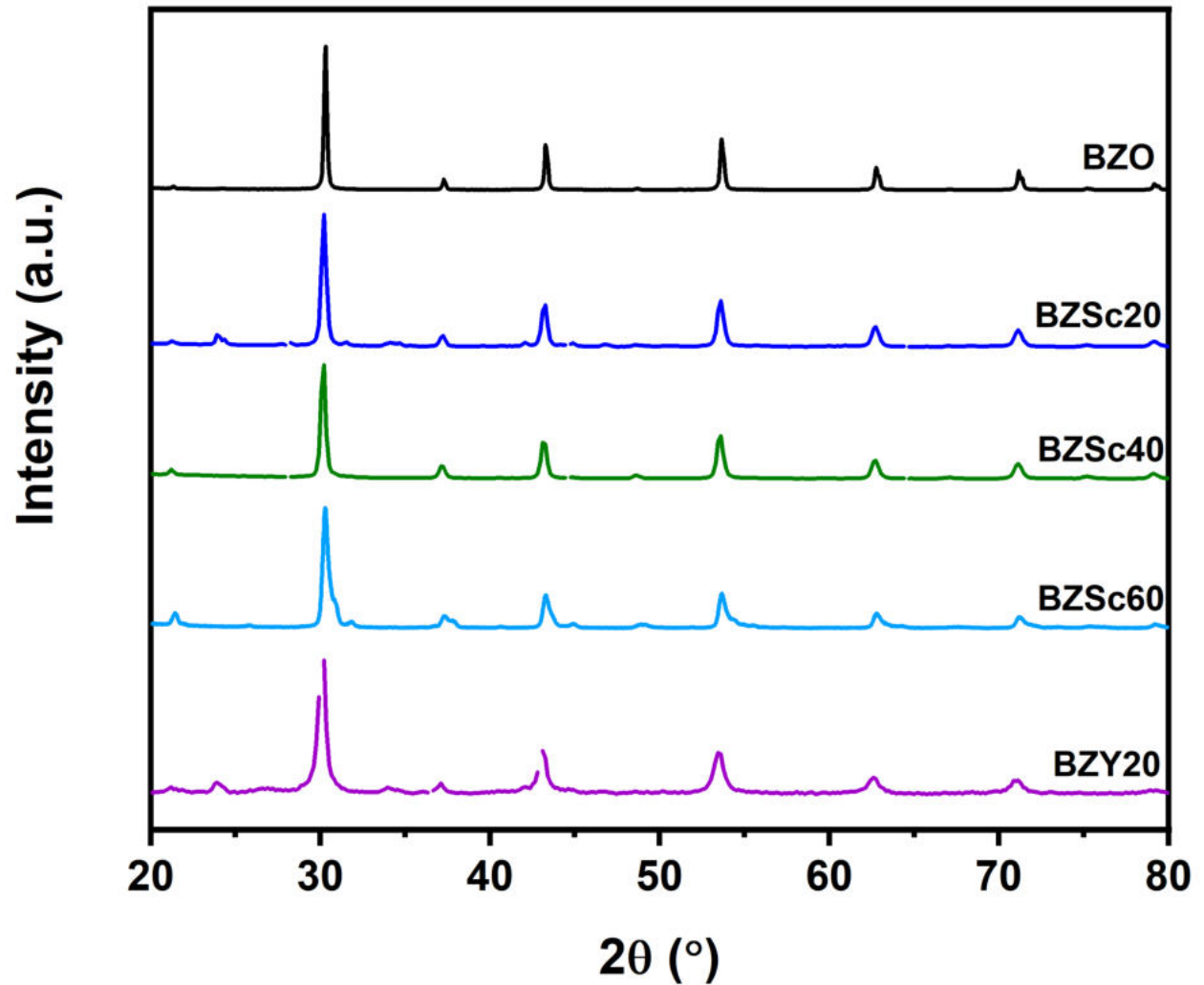
changes with respect to dry samples



(Figure from *Chem. Mater.* 2015, 27, 6660–6667)

Several techniques are used to investigate where protons are trapped, among them NMR and XRD

X-ray Diffraction



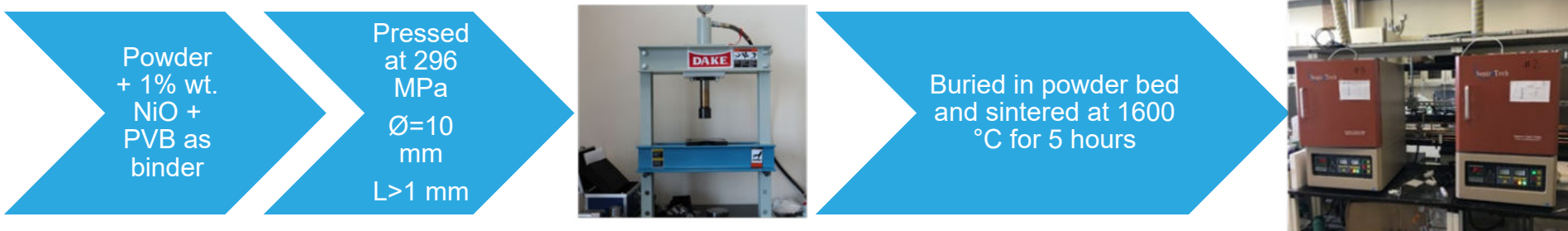
XRD diffraction shows the most pure phase; some phase shifts observed in the doped specimens

Metal oxide sample preparation

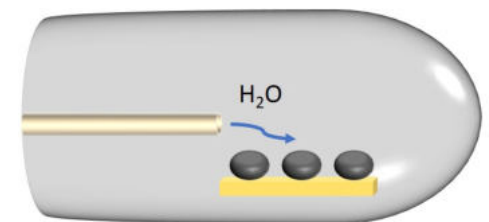
- BZO, 20% Sc-BZO, 40% Sc-BZO, 60% Sc-BZO and 20% Y-BZO were prepared by the solid-state reaction method



- Specimens for PAL were prepared by dry pressing. After sintering, one surface of the pellet was polished to study surface effects



- Hydration of the samples was performed at 300 °C in Argon atmosphere containing 10% H_2O for 24 hours

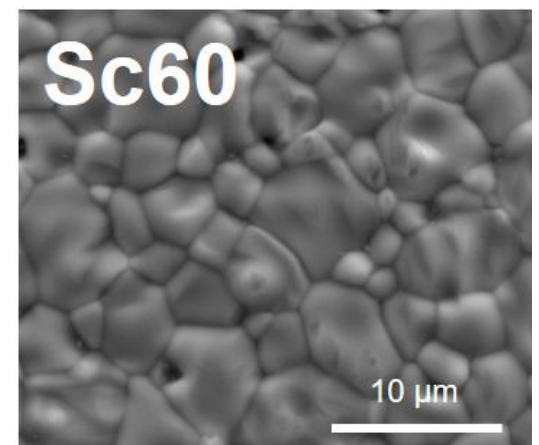
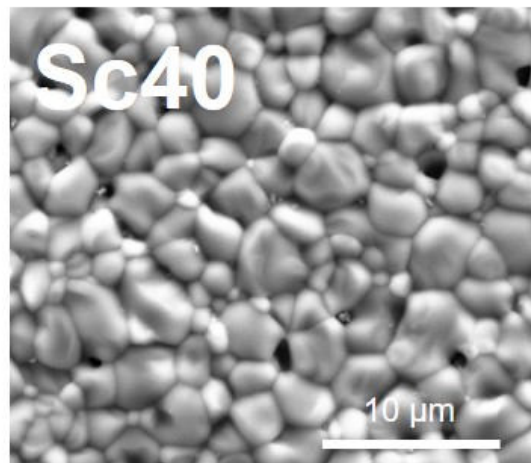
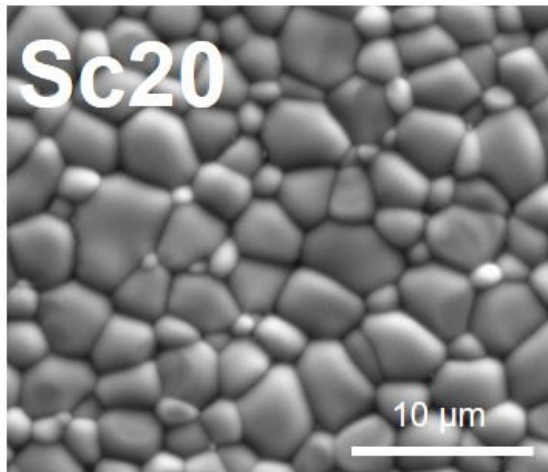
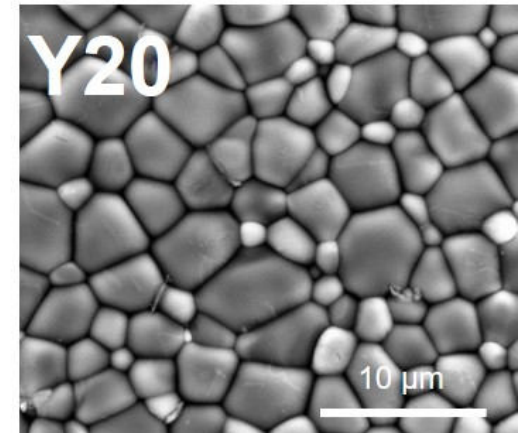
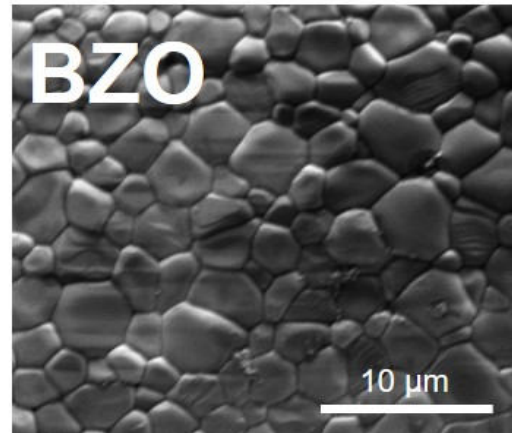


Sample characterization

After sintering, all samples showed density higher than 90%

SEM images show surfaces composed of big and small grains; but rather in micro-meter range, than nano-meter range

Material	ID	Density %
BaZrO_3	BZO	98.6 ± 0.6
$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-5}$	Y20	97.9 ± 0.3
$\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{3-5}$	Sc20	96.9 ± 0.7
$\text{BaZr}_{0.6}\text{Sc}_{0.4}\text{O}_{3-5}$	Sc40	95.2 ± 0.1
$\text{BaZr}_{0.4}\text{Sc}_{0.6}\text{O}_{3-5}$	Sc60	90.4 ± 0.1



Specimens measured by use of PAL

Three series of PAL measurements were conducted

series 1

- 1) Electrolyte with no dopant – reference: BaZrO_3 [BZO]
- 2) Electrolyte with different amount of the same dopant: 20% Sc [Sc20] and 40% Sc [Sc40] BaZrO_3

series 2

- 1) Electrolyte with 60% of Sc dopant [Sc60]
- 2) Electrolyte with 20% Sc- hydrated [Sc20H]

series 3

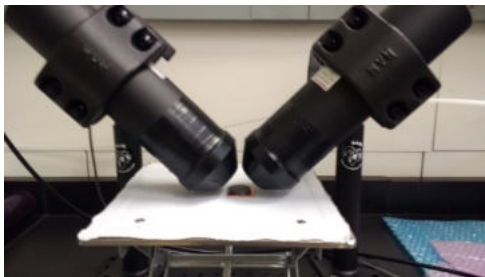
- 1) Hydrated electrolyte with no dopant: BaZrO_3 [BZOH]
- 2) Electrolyte with 20% of Ytrium 20% Y [Y20]
- 3) Electrolyte with 20% of Ytrium – hydrated [Y20H]

Each specimen type was represented by three pellet samples

PAS New Digital System and Upgrade Capabilities

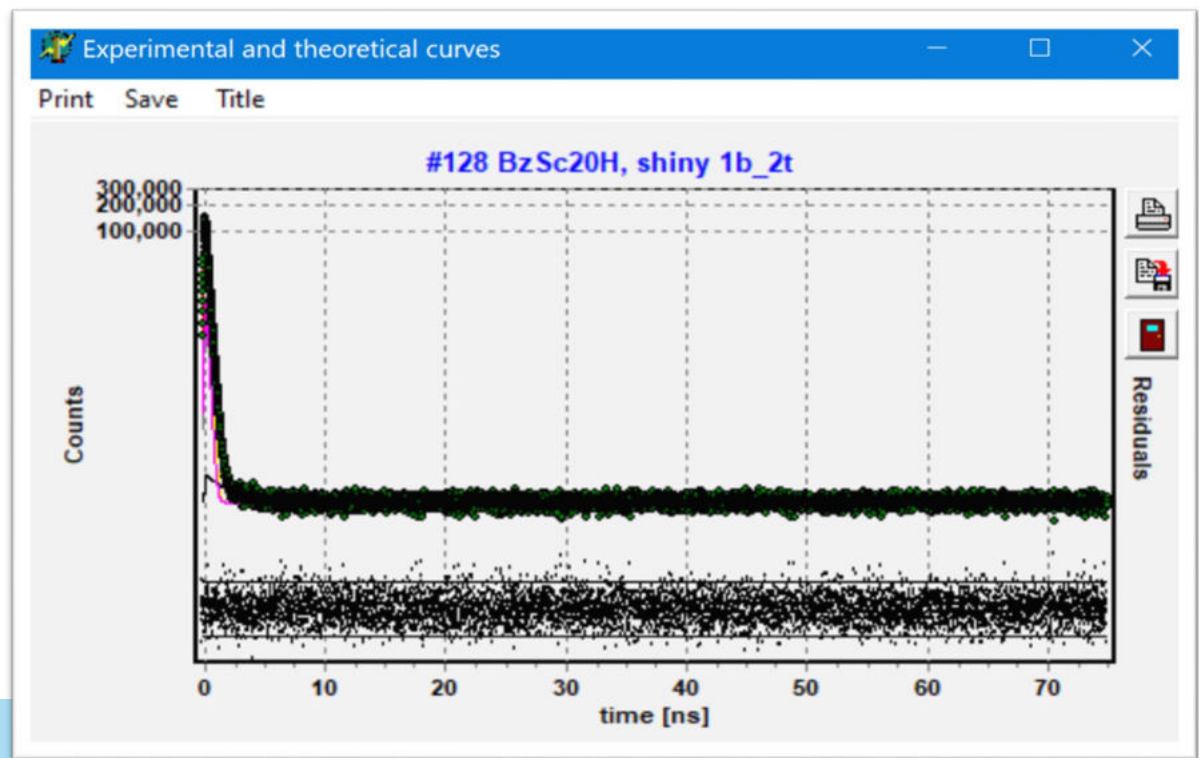
State of the art digital equipment from TechnoAP, Japan was purchased recently, with three PAS technologies in one module:

- **PAL** (Positron Annihilation Lifetime)
- **CDBS** (Coincidence Doppler Broadening Spectroscopy)
- **AMOC** (Age-momentum Coincidence Spectroscopy)



PAL laboratory (INL – IRC B-1) with modular digital system, purchased in Fall 2019, upgraded in October 2020
CDB is being installed now

Typical PAL spectrum for oxide metal: BZO with SC20H (hydrated)



#128 BzSc20H, shiny 1b_2t

Analysed between channels 980 and 8192. Calibration=0.01042 ns/chann.

Total counts=5219525

Bkgr./signal=9.96%

Fit's variance =0.9970

Date: 6/21/2021 11:30:19 AM

SAMPLE:

intensities [%]	lifetimes [ns]	dispersions [ns]
44.2(1.3)	0.146(0.044)	0.0000
55.5(1.3)	0.227(0.047)	0.0000
0.38(0.14)	1.72(0.27)	0.0000

SOURCE :

contribution	20.0000 [%]
intensities [%]	lifetimes [ns]
50.0000	0.2604
50.0000	0.1560

ZERO CHAN. 994.0457(0.0099) BACKGROUND 72.06(0.32) [Counts]

RESOLUTION CURVE :

ESG fract. (%)	Shift (chnns)	FWHM (ns)	tau(left) (ns)	tau(right) (ns)
100.0000	0.0000	0.1715	0.0000	0.0000

Kansy LT9.2 program used for PAL analysis

PAL resolution is about 170 ps

Matrix effect taken into account

Na-22 source in 0.5 mil Ti

How positrons behave in metal oxides ?

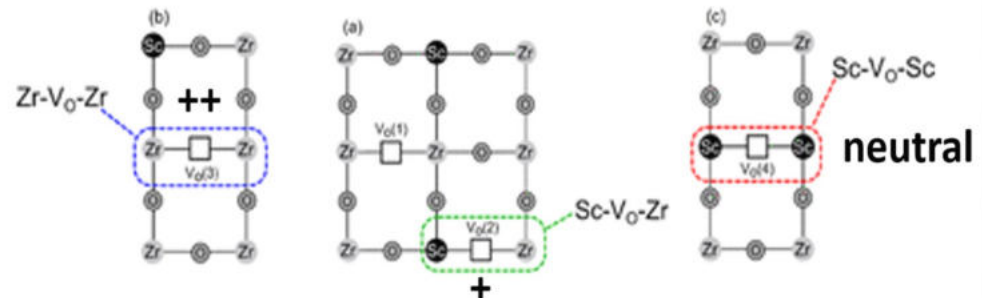
According to the literature:

Predictions versus experiment ?

- **Point defects in Zr^{+4}** (negative voids) will attract positrons (deep traps)
- **Point defects in dopants** (Y^{+3} , Sc^{+3} neutral defects) – could also attract positrons but we will have shallow traps
- **Grain boundary misfit trapping** (also point defects) may occur at about 180-200 ps, but this would happen mainly in nano-grains, we deal here with micro-meter grains
- **Triple point volume defects**, at about 370 ps, but its intensity gets lower with high density
- Point defects in place of O_2 (positive voids) are present but they would not trap positrons, so positrons don't see them.
- There is also significant positronium formation in porous metal oxides (before sintering) with the lifetime at about 30 ns, pore size : 2.5-3 nm

[1] J.E. Garay, S.C. Glade., P. Asoka-Kumar and others, *J. of Applied Physics*, **99**, 024313, (2006)

[2] I. Prohazka, J. Cizek, O. Melikhova, and others, *J. AM. Ceram. Soc.* **97**, 982-989, (2014)



PAL Initial Results – series 1: BZO pure and with Sc dopants

Specimen	T_1 [ns]	dT_1	I_1 [%]	dI_1	T_2 [ns]	dT_2	I_2 [%]	dI_2	T_3 [ns]	dT_3	I_3 [%]	dI_3
BZO 1B-2T S	0.1563	0.0006	64.83	0.25	0.2510	0.0026	34.77	0.37	1.843	0.012	0.417	0.107
Sc-20 1B-2T S	0.1557	0.0040	55.23	5.20	0.2390	0.0061	44.40	5.21	1.843	0.136	0.387	0.060
Sc-40 1B-2T S	0.1563	0.0006	55.64	1.28	0.2370	0.0026	44.03	1.31	1.957	0.025	0.350	0.018
BZO 2B-3T NS	0.1625	0.0007	73.06	0.79	0.2645	0.0092	26.49	1.01	2.000	0.057	0.450	0.226
Sc-20 2B-3T NS	0.1615	0.0021	63.35	2.05	0.2540	0.0071	36.05	2.19	1.930	0.028	0.590	0.141
Sc-40 1B-2T NS	0.1620	0.0028	68.21	3.10	0.2593	0.0007	31.27	3.08	1.965	0.007	0.520	0.006

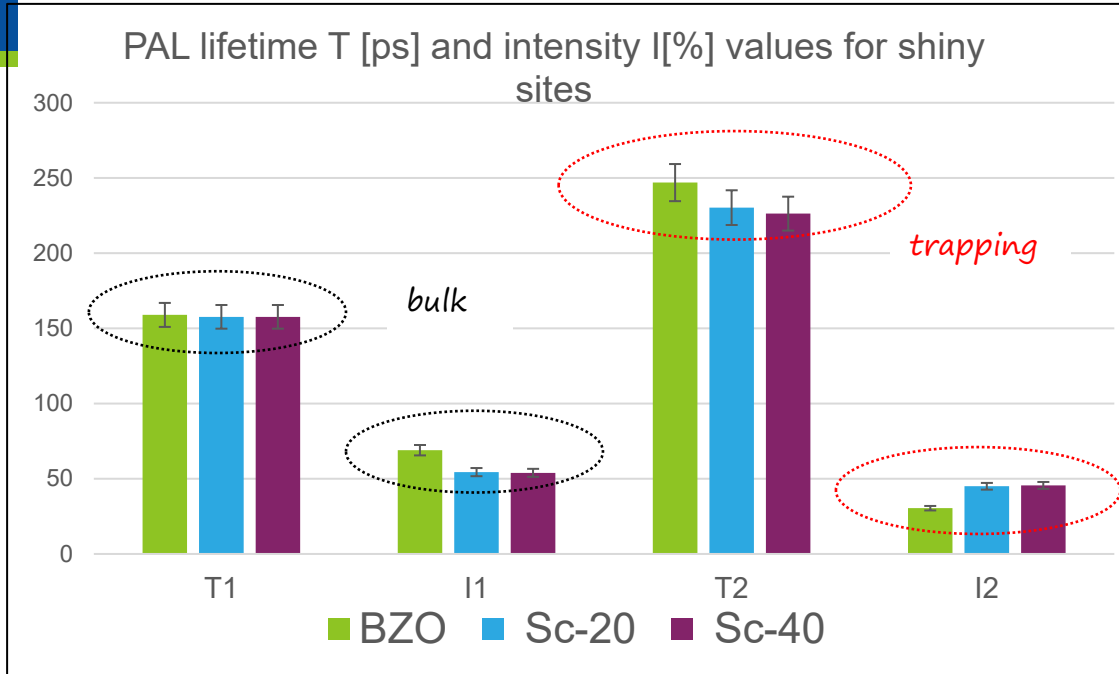
PAL Average values for all three specimen types – for [S] shiny (polished) versus [NS] (not polished) sites – without source correction

specimen	T_1 [ns]	dT_1	I_1 [%]	dI_1	T_2 [ns]	dT_2	I_2 [%]	dI_2	T_3	dT_3	I_3 [%]	dI_3
BZO 1B-2T S	0.159	0.001	69.00	0.60	0.247	0.005	30.47	0.75	1.85	0.01	0.52	0.14
Sc-20 1B-2T S	0.158	0.006	54.48	9.11	0.230	0.008	45.05	9.08	1.86	0.13	0.48	0.08
Sc-40 1B-2T S	0.158	0.001	53.97	2.84	0.226	0.004	45.60	2.80	1.97	0.03	0.43	0.02
BZO 2B-3T NS	0.166	0.000	80.20	0.28	0.270	0.014	19.23	0.53	2.00	0.04	0.56	0.28
Sc-20 2B-3T NS	0.166	0.003	68.25	3.32	0.253	0.011	31.05	3.46	1.93	0.03	0.74	0.18
Sc-40 1B-2T NS	0.157	0.004	51.05	4.74	0.225	0.001	48.55	4.74	1.96	0.01	0.42	0.01

PAL Average values for all three specimen types – for S vs NS sites – with source correction.

- BZO has higher intensity of bulk annihilation I_1 lower intensity of trapping I_2 but longer trapping time, T_2 - hypothesis: dopants increase electron density in the site of the trap, but higher electron density around trap also attract more positrons
- In non-polished specimens I_3 and T_3 increase; hypothesis: there are some surface Ps states present

PAL Results – initial Comparison BZO vs Sc dopant concentration



Bar diagram with T1, I1 and T2 and I2 values for shiny sides of the specimens, with 5% of standard error

T-test	T ₁	I ₁	T ₂	I ₂
BZO shiny / Sc 20	0.7096	0.0511	0.0436	0.0503
BZO shiny / Sc 40	0.2051	0.0009	0.0058	0.0008
Sc 20 versus Sc 40	1.0000	0.9307	0.4981	0.9245

PAL T-test for BZO, versus Sc-20 and Sc-40 shows that BZO intensities for bulk and trapping as well as trapping lifetime are significantly different; and there might be a tendency to lower trapping time with dopant concentration but the initial hypothesis could not be rejected on level of 5% significance (less than 0.05)

PAL measurements were continued – including Sc-60, Y-20, and hydrated samples

Material	ID	Density %	Diameter shrinkage (%)	Thickness shrinkage (%)
$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$	Y20 #1	97.7	18.3	17.7
$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$	Y20 #2	97.7	18	19.7
$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$	Y20 #3	97.6	19.1	20.1
$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$	Y20 H #2	98.1	18.2	21.7
$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$	Y20 H #2	98.2	18.5	16.9
$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$	Y20 H #3	98.3	18.4	26.2
$\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{3-\delta}$	Sc20 #1	98.0	17.7	15.0
$\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{3-\delta}$	Sc20 #2	97.5	17.8	15.0
$\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{3-\delta}$	Sc20 #3	96.4	17.7	10.0
$\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{3-\delta}$	Sc20 H #1	97	18.2	22
$\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{3-\delta}$	Sc20 H #2	96.4	17.8	19.2
$\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{3-\delta}$	Sc20 H #3	96.3	18.3	23

***Hydration procedure:** after polishing, samples were dried at 700 C for 0.5 hrs and then cooled down to 300 C with 10% H₂O in Ar. The hydration was maintained for 24 hrs.*

***Density** measurements were performed before hydration*

***BZO doped with Sc-60** was brittle, less stable thermally and mechanically than other specimens; it disintegrates in the presence of steam, one of the samples shattered like glass after the measurement*

Average PAL values with sample standard deviation for series 1-4 with source correction – for polished sites inwards

specimen	T_1 [ns]	dT_1	I_1 [%]	dI_1	T_2 [ns]	dT_2	I_2 [%]	dI_2	T_3	dT_3	I_3 [%]	dI_3
BZO S	0.158	0.002	68.37	1.35	0.246	0.005	31.10	1.40	1.768	0.170	0.53	0.11
Sc20 S	0.158	0.004	56.74	6.46	0.232	0.006	42.81	6.45	1.835	0.090	0.46	0.10
Sc40 S	0.158	0.001	53.97	2.84	0.226	0.004	45.60	2.80	1.973	0.030	0.43	0.02
Sc60 S	0.154	0.000	53.40	0.85	0.231	0.002	46.20	0.85	1.770	0.020	0.39	0.02
BZOH S	0.153	0.003	83.48	3.49	0.238	0.008	16.12	3.48	1.725	0.160	0.41	0.01
Sc20H S	0.150	0.006	50.35	6.88	0.231	0.006	49.25	6.89	1.683	0.130	0.41	0.05
Y20 S	0.151	0.005	45.92	2.94	0.248	0.004	53.63	3.01	1.734	0.080	0.45	0.06
Y20H S	0.151	0.001	45.42	2.80	0.260	0.005	54.06	3.05	1.945	0.160	0.54	0.27

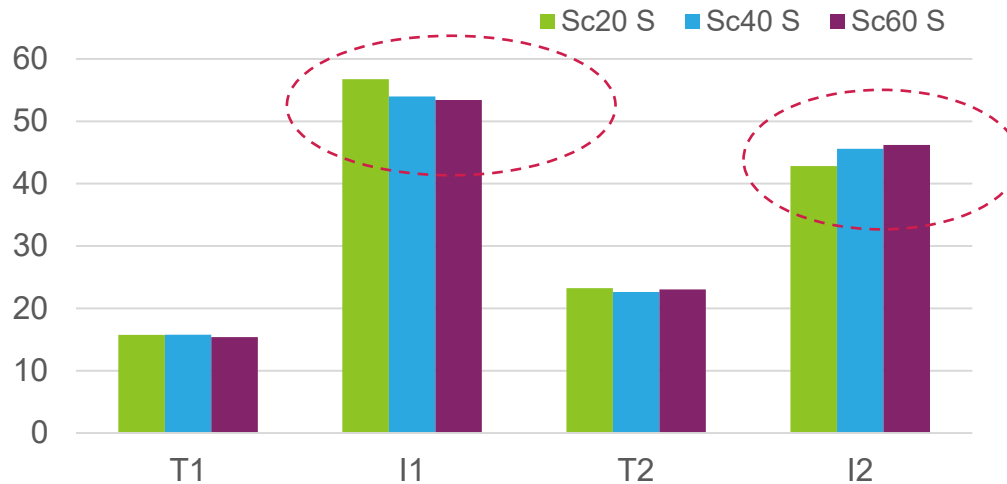
ranges

- $T_1 = 151$ - 158 ps, $I_1 = 45$ - 84 %; bulk lifetime and intensity
- $T_2 = 226$ - 260 ps, $I_2 = 16$ - 54 %; trapping lifetime and intensity
- $T_3 = 1.68$ - 1.97 ns, $I_3 = 0.39$ - 0.54 %; surface positronium states, low intensity since the samples are very dense; no Ps formation inside

The mechanism of trapping is completely different in BZO pure samples compared to doped; there are just in not good trapping sites in pure metal oxides therefore the annihilation in the bulk is so significant in BZO and it increases with hydration – added density

PAL bulk and trapping lifetimes comparison for specimens with different level of Sc doping

PAL - level of doping with Sc



Doping with Sc increases trapping intensity.

Bulk intensity I_1 , is decreasing with Sc dopant concentration while I_2 , trapping intensity is increasing. Changes in the lifetimes, if specimen is already doped are not significant.

The difference in I_1 and I_2 intensities between Sc20 and Sc40 are significant. While the same trend is continuing for Sc60, the difference in the values between Sc40 and Sc60 is less than two standard deviations; so this effect is not-linear.

No Ps formation inside in dense and sintered at high temp specimens.

specimen	T_1 [ns]	dT_1	I_1 [%]	dI_1	T_2 [ns]	dT_2	I_2 [%]	dI_2	T_3	dT_3	I_3 [%]	dI_3
BZO S	0.158	0.002	68.37	1.35	0.246	0.005	31.10	1.40	1.768	0.170	0.53	0.11
Sc20 S	0.158	0.004	56.74	6.46	0.232	0.006	42.81	6.45	1.835	0.090	0.46	0.10
Sc40 S	0.158	0.001	53.97	2.84	0.226	0.004	45.60	2.80	1.973	0.030	0.43	0.02
Sc60 S	0.154	0.000	53.40	0.85	0.231	0.002	46.20	0.85	1.770	0.020	0.39	0.02

PAL bulk and trapping lifetimes for non-hydrated/hydrated specimens

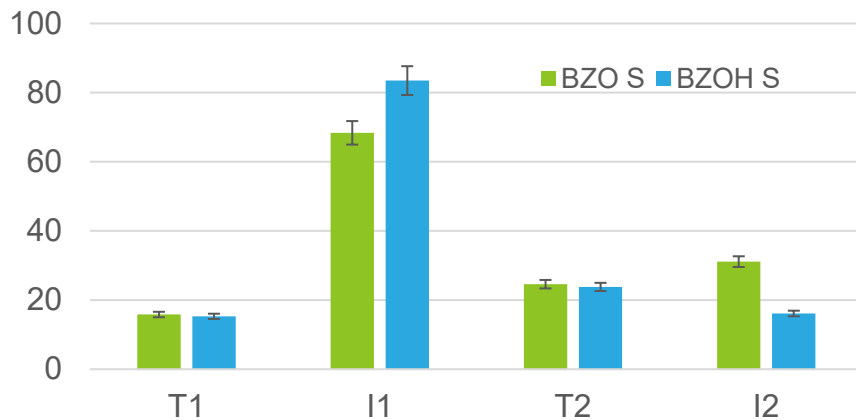
The mechanism of positron interaction is different at BZO than in the dopants.

In BZO hydration causes significant decrease in trapping fraction (50%) & increase in bulk annihilation.

For Sc20 trapping fraction increases with hydration
For Y20 trapping lifetime increases with hydration

Trapping lifetime for Sc20 is lower than for Y20, the mean lifetimes are also significantly different. It is related to their atoms size, density and electron structure

PAL values for BZO with/without extra hydrogen



specimen	T1	I1	T2	I2	T3	I3	mean lifetime
BZO S	0.158	68.37	0.246	31.10	1.768	0.53	19.394
BZO H S	0.153	↑ 83.48	0.238	↓ 16.12	1.725	0.41	17.297
Sc20 S	0.158	56.74	0.232	42.81	1.835	0.46	19.717
Sc20 H S	0.150	↓ 50.35	0.231	↑ 49.25	1.683	0.41	19.619
Y20 S	0.151	45.92	0.248	53.63	1.734	0.45	21.011
Y20 H S	0.151	45.42	↑ 0.260	54.06	1.945	0.54	21.885

	Sc	Ti	V
19	173	132	
16	253	206	
	Y	Zr	N
19	189	142	
10	278	228	
	La	Hf	Ta

Conclusions

- The PAL analysis showed **drastically different mechanism** of positron reaction in the BZO and a response to hydration compared to the specimens with dopants.
- BZO specimens: **more bulk annihilation** and its fraction increases for hydrated samples; while in doped samples there is more trapping and trapping increases with hydration.
- With **more dopant concentration trapping intensity is increasing** although this effect is non-linear. The most increase is in the initial stages of doping.
- Trapping lifetime is significantly different in Sc versus Y doped specimens, which is in agreement with the literature and their chemistry.
- Positronium can be formed on the surface of oxide metals, and this effect is more significant when non-polished sides are inwards, still it is less than 1% since the specimens are sintered and dense.

BZO, Sc and Y-doped metal oxides have different signatures

Multi-variate Analysis (MVA)

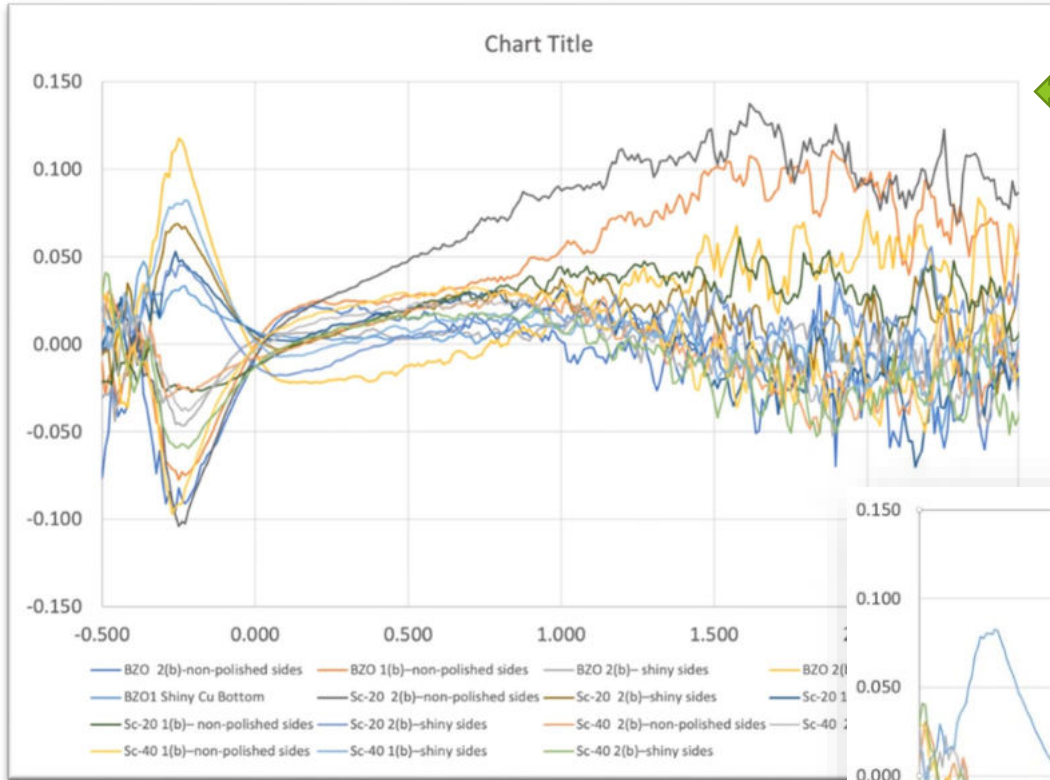
- Establish the baseline non-defected/non-doped samples, start with reference samples, go through the process of change
- Methods such as principal components analysis (PCA) and regression (PCR) and partial least squares (PLS) will be applied to the PAS lifetime and DB spectra and related to broader bulk properties of the materials.
- Training and Verification sets will be generated based upon known properties.

$$A = KC$$

- While the algorithms are more complex, the basic form for PCA/R and PLS is represented by the simple least squares equation shown above.
- In this case, A is a vector representing a spectrum or matrix of spectra.
- C is the “concentration” of the various properties that are represented in the spectrum/spectra of A, e.g. properties may include density, hardness, porosity, etc.
- K is a vector(s) of coefficients that relate the spectra in A (response strength) to the “concentrations” in C.
- Pretreatment of the spectral data in A (e.g. derivatives, rationing, etc.) can enhance the differences and increase the correlations.

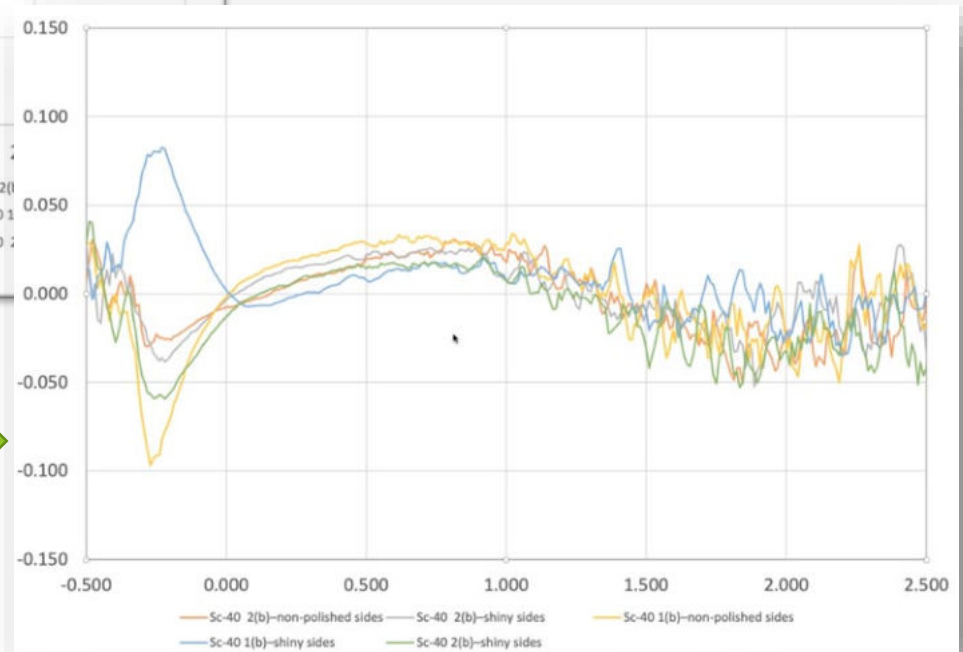
Multi-variate Analysis (MVA)

Mathlab can be used for MVA analysis

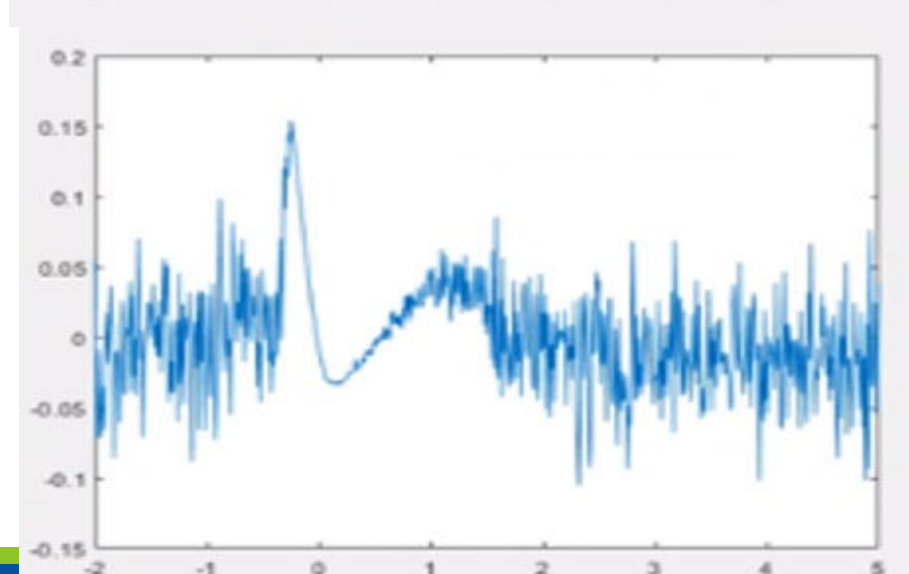
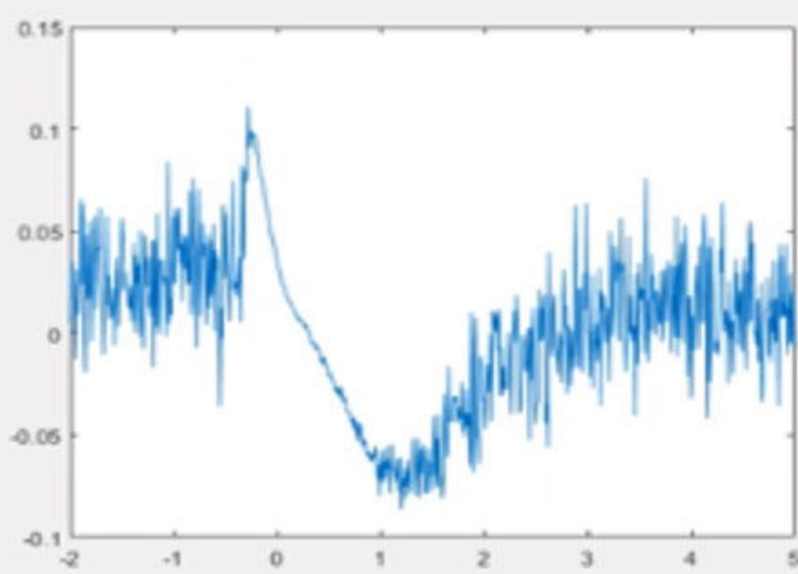
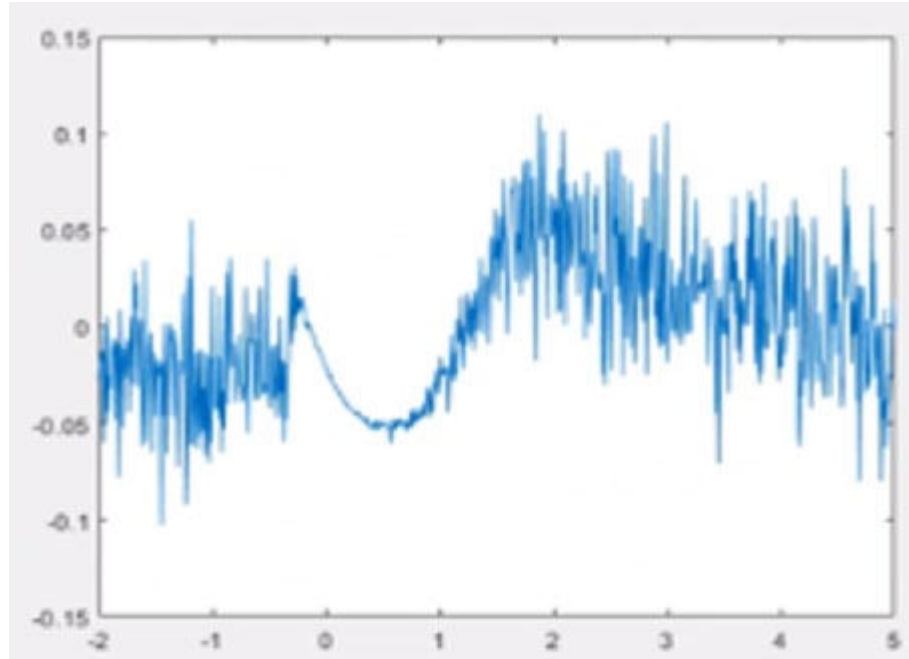
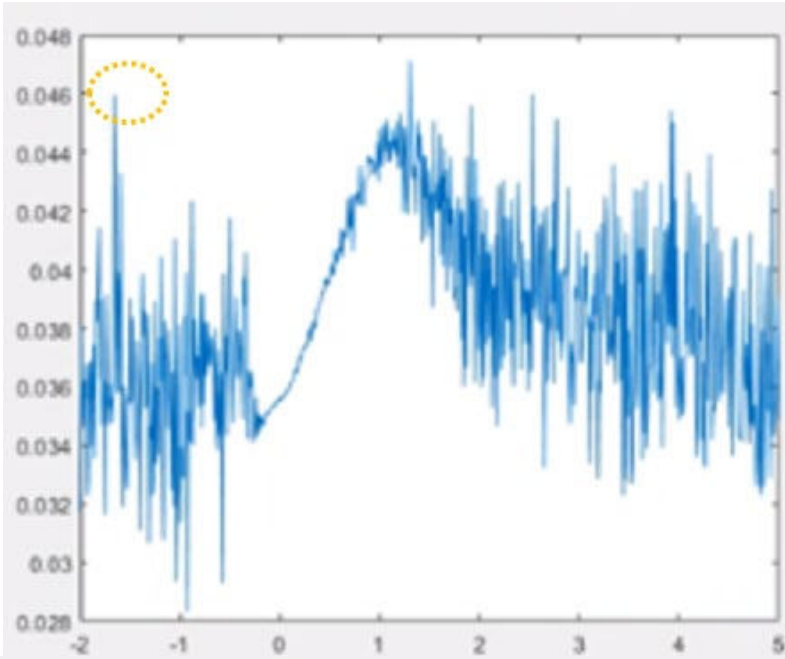


Variety of metal oxides

Sc-40 subgroup

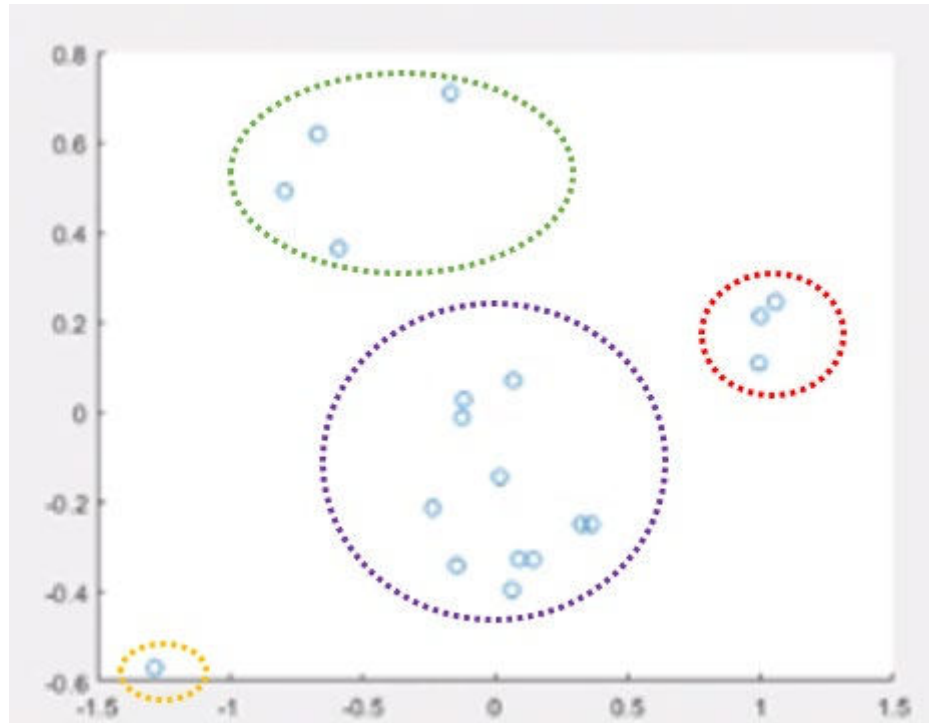


MVA –extract four independent factorials and find the groupings



Find groupings/clusters in metal oxides

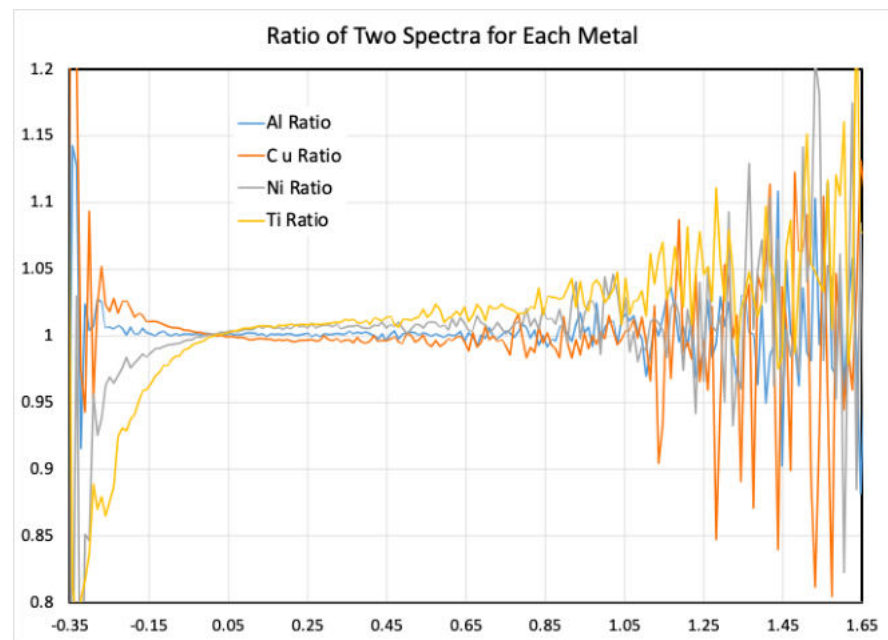
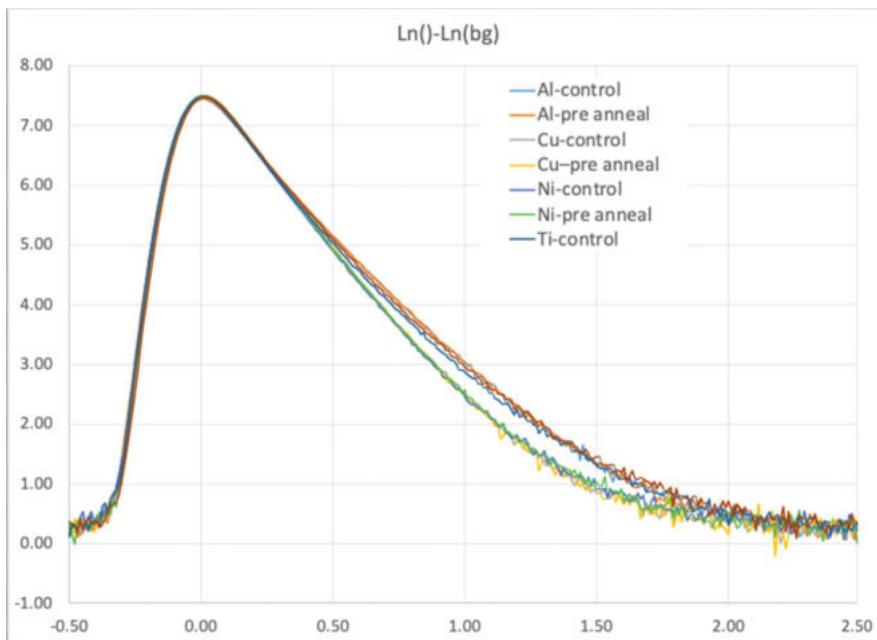
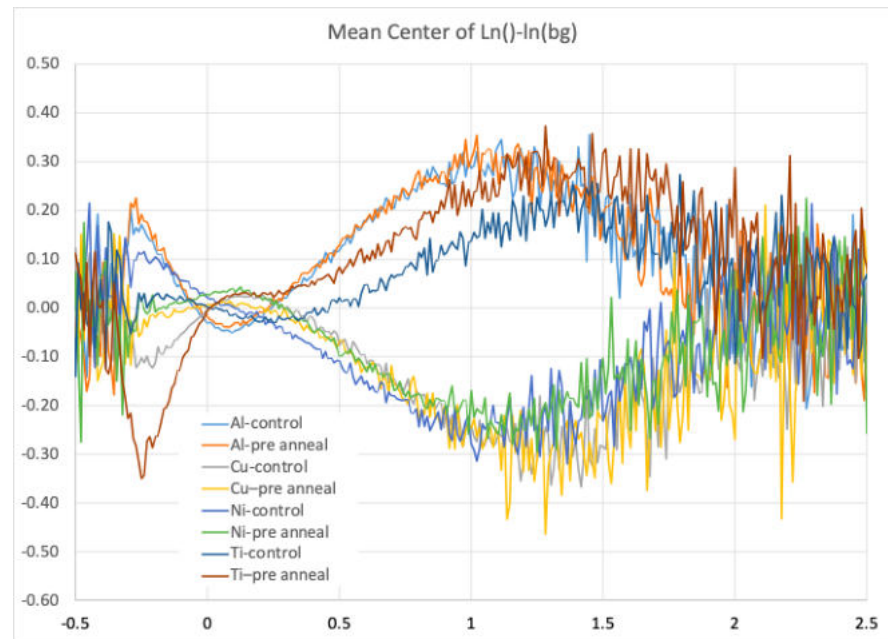
For factorials 2 and 3



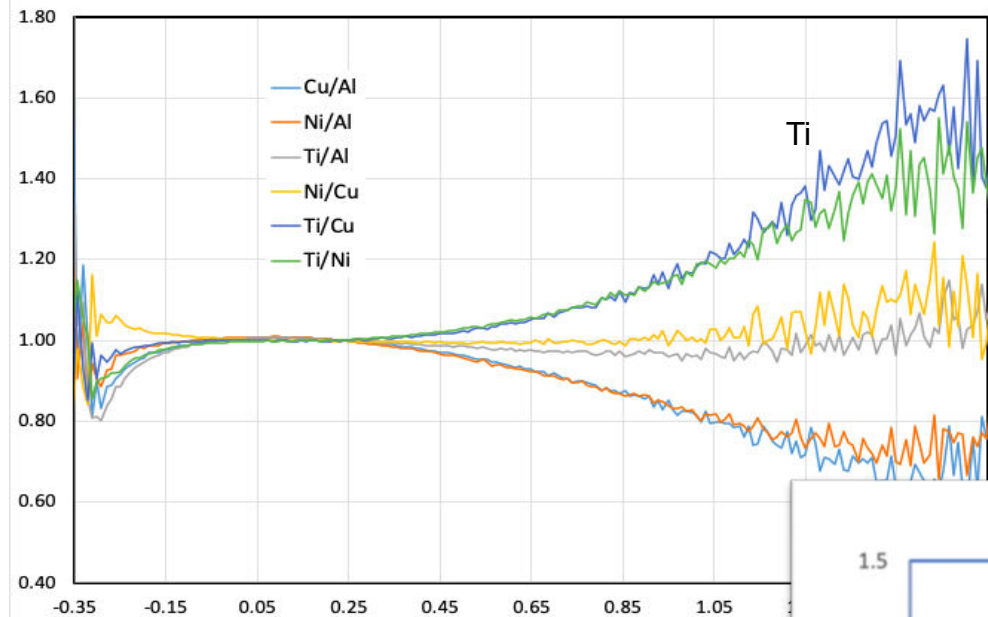
This technique can show which independent components are correlated, associated or linked to each other



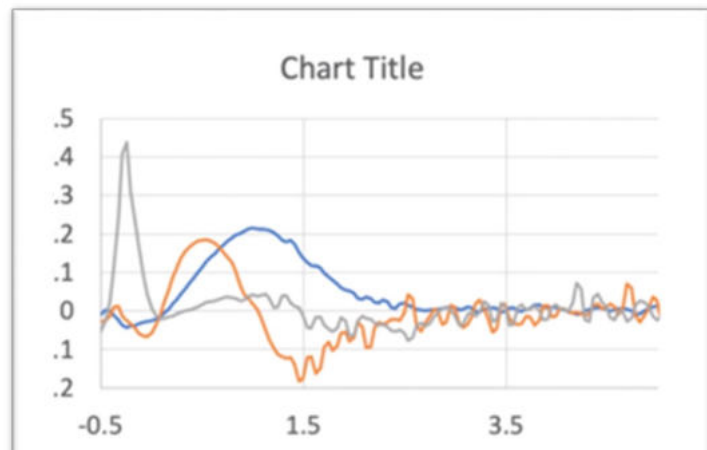
Metals annealing – experiment conducted to find the matrix effect for Ti, but also Cu, Ni and Al



Metal Ratios

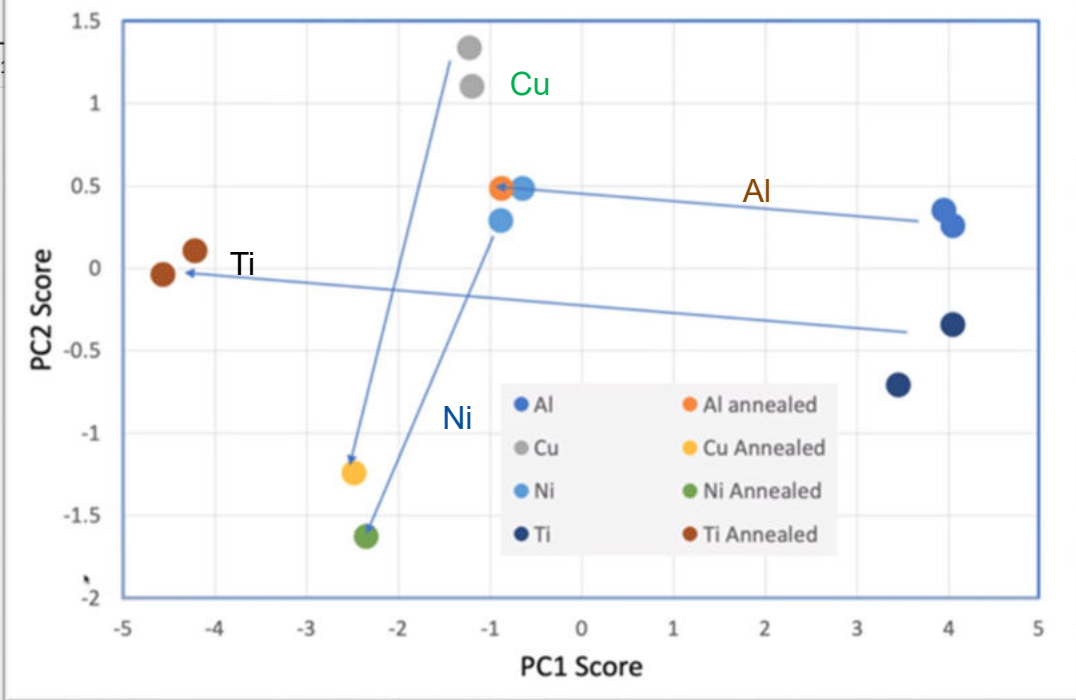


Principal components scores



**Metals annealing –
changing the scores**

Annealed Metals



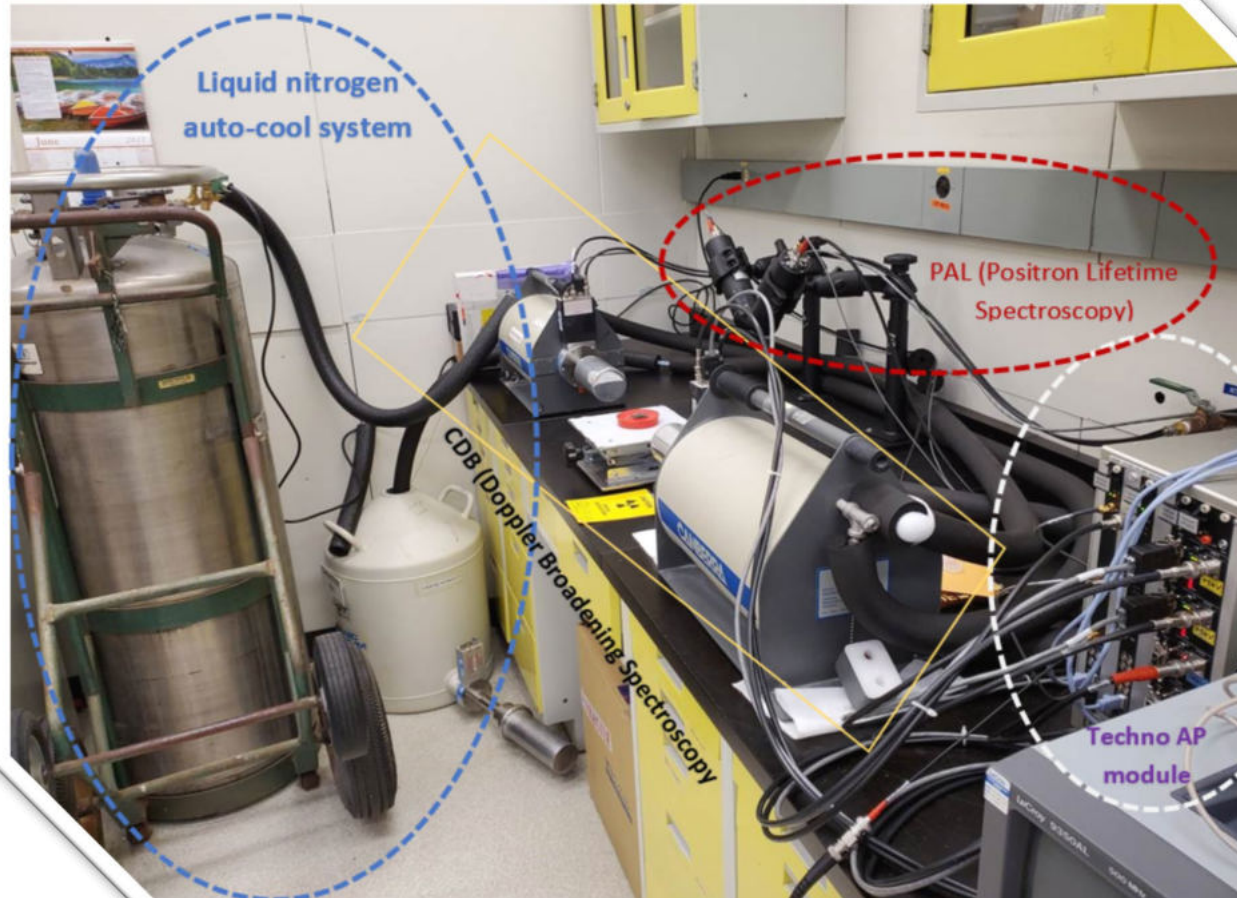
Plans for future

- Perform Coincidence Doppler Broadening (CDB) measurements for the same specimens. The DBS measurements have more sensitivity towards momentum distribution and the effect of different charged states. It is also sensitive to oxygen vacancies.
- Work on relationship between trapping lifetimes and intensities and how they correspond to the void type.
- Attempt to produce BZO doped with materials from a different part of periodic table.
- Perform measurements on specimens that have not been sintered, or have been sintered in lower temperatures than 1500 C.
- Carry out multi-variate analysis to check whether it would allow to extract some properties not visible by use of PAL analysis.

Coincidence Doppler Broadening Measurements with auto-cool system

Positron Annihilation Spectroscopies in IRC B-1 lab

Jaga Urban-Klaehn, August 4, 2021



CDB Recognizes charged state and voids chemistry/electron state density

1. PAL (Positron Lifetime Spectroscopy) – developed in Fall 2019, upgraded in 2020.
2. CDB (Coincidence Doppler Broadening Spectroscopy) – developed in summer 2021
3. TechnoAP module – purchased in Fall 2019.
4. Liquid Nitrogen auto-cool system – developed in summer 2021

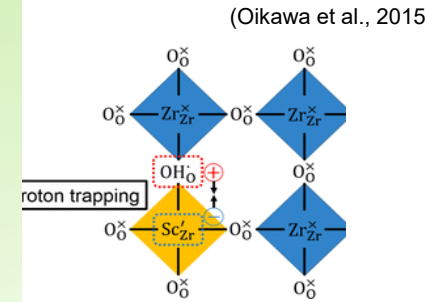


Thank you for your attention

Appendix

Proton trapping:

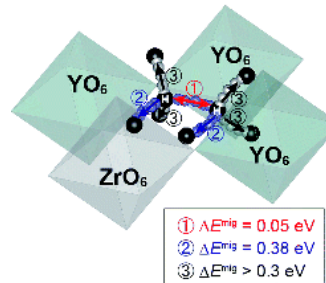
- Localization of oxygen vacancy is relevant because once the oxygen vacancy is hydrated, the proton on that position could experience an attraction by the dopant atom
→ proton trapping
- Proton trapping reduces the proton conductivity
- Proton trapping is a function of doping %



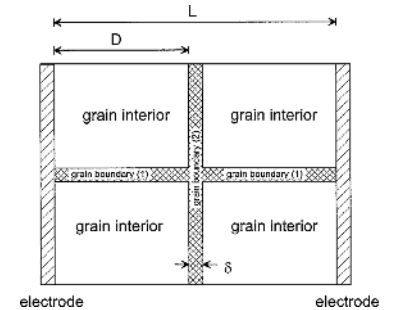
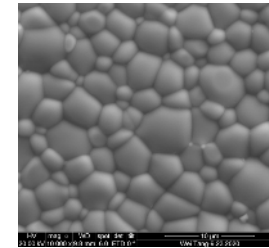
Defect clusters:

- Dopant atoms could form association
- Dopant clusters increases proton trapping

(d) Triangular Y configuration



(Toyoura et al., 2018)



(Haile et al., 2001)

Grain boundary:

- Oxygen vacancies tend to segregate at the grain boundary
- Space – charge region is formed
- The proton conductivity can be lowered due to the high resistance at the grain boundaries

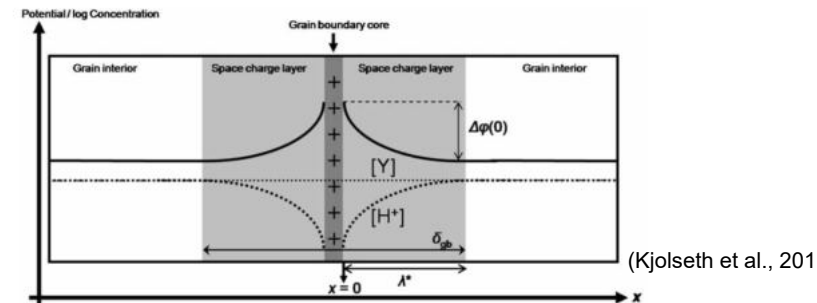


Fig. 1. Schematic grain boundary consisting of a positive core charge compensated by two adjacent space-charge layers. Values of x are defined such that $x=0$ at the interface between the space-charge layer and the grain boundary core, while far into the grain interior $x=\infty$. The dotted lines represent concentration profiles in the space-charge layer for the protons and the acceptor dopant under the Mott-Schottky approximation, while the unbroken line represents the potential profile. The Schottky barrier height potential difference is also indicated.

Data Reproducibility – series 1-4

series	ID	specimen	T1	I1	T2	I2	T3	I3	<t>
series 1	29	BZO 1B-2T S	0.159	69	0.245	30.5	1.85	0.44	19.26
	35	BZO 2B-3T S	0.158	68.4	0.243	31.2	1.86	0.44	19.21
	43	BZO 2B-3T S	0.16	69.6	0.253	29.7	1.84	0.68	19.90
series 3	163	BZO 1B_2T S	0.156	66.48	0.243	32.99	1.52	0.54	19.21
		<i>mean</i>	0.158	68.37	0.246	31.10	1.77	0.53	19.39
		<i>sdvevas</i>	<i>0.002</i>	<i>1.352</i>	<i>0.005</i>	<i>1.403</i>	<i>0.165</i>	<i>0.114</i>	<i>0.339</i>
		<i>error</i>	<i>0.011</i>	<i>0.020</i>	<i>0.019</i>	<i>0.045</i>	<i>0.093</i>	<i>0.216</i>	<i>0.017</i>
	30	Sc-20 1B-2T S	0.156	51.5	0.226	48.1	1.72	0.4	19.59
	36	Sc-20 2B-3T S	0.164	64.7	0.24	34.83	1.87	0.47	19.85
	44	Sc-20 2B-1T S	0.153	47.23	0.225	52.21	1.98	0.56	20.08
series 4	442	Sc20, S 3B-2T	0.157	61.2	0.238	38.2	1.82	0.59	19.77
	443	Sc20, S 3B-2T	0.157	56.3	0.23	43.3	1.83	0.42	19.57
	444	Sc20, S 1B-2T	0.165	70.3	0.269	28.74	1.93	0.96	21.18
	445	Sc20, S 1B-3T	0.158	59.5	0.235	40.2	1.79	0.33	19.44
		<i>mean</i>	0.159	58.68	0.238	40.80	1.85	0.53	19.93
		<i>sdvevas</i>	<i>0.004</i>	<i>7.817</i>	<i>0.015</i>	<i>7.937</i>	<i>0.087</i>	<i>0.209</i>	<i>0.59</i>
		<i>error</i>	<i>0.027</i>	<i>0.133</i>	<i>0.063</i>	<i>0.195</i>	<i>0.047</i>	<i>0.392</i>	<i>0.03</i>

Calculate mean, standard deviation, standard error, eliminate outliers

References

1. [TechnoAP PAS equipment, http://www.techno-ap.com/index_e.html](http://www.techno-ap.com/index_e.html)
2. [J. Kansy, Microcomputer program for analysis of positron annihilation lifetime spectra, Nucl. Instrum. Methods Phys. Res., Sect. A. 374 \(1996\) 235–244. doi:10.1016/0168-9002\(96\)00075-7.](#)
3. Garay, J.E., Glade S.C and others, Characterization of densified fully stabilized nanometric zirconia by positron annihilation spectroscopy; Journal of Applied PhysSc, 99(2), 2006.
4. Prohazka I, Cizek J., Melikhowa O., and others, “Positron Annihilation Study of Zircona Nnopowders and nanoceramiSc Stailized by Magnesia and Ceria, J. American Ceram. Soc. 97(1), 2014.

CDS spectrum

