# Structure relations in the solid solutions of hafina/zirconia

Spotlight on Germany's Young Crystallographers

Melanie Nentwich

München, 14.-17.03.2022

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## Structure relations in the solid solutions of $Hf_xZr_{1-x}O_2$.

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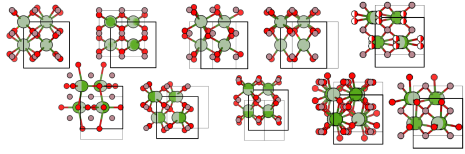
See also Posters P55 and P90!

DESY.

## Motivation

- potentially ferroelectric
- compatible with silicon technology
- low toxicity
- great perspectives in semiconductor applications
- chemical simplicity, BUT large variety of different phases



## Abstract


- complete list of 10 experimentally and 13 theoretically reported phases
- symmetry relations presented in a Bärnighausen-like tree (BHLT)
- partially: severe atomic shifts involved

| auxiliary type | | atomic shift | | | after *r* | | | |
|---|---|---|---|---|---|---|---|---|
| site | | $x/a$ | $y/b$ | $z/c$ | site | $x/a$ | $y/b$ | $z/c$ |
| O | $4a$ | 0 | $1/8$ | $1/8$ | $4a$ | 0 | $3/8$ | $1/8$ |
| | | 0 | $1/8$ | $-3/8$ | | 0 | $7/8$ | $1/8$ |
| | | 0 | $-1/8$ | $-3/8$ | | 0 | $5/8$ | $5/8$ |
| | | 0 | $-1/8$ | $-3/8$ | | 0 | $1/8$ | $5/8$ |

- detailed comparison of the structure types
- application: transforming reflection indices during phase transition with BHLT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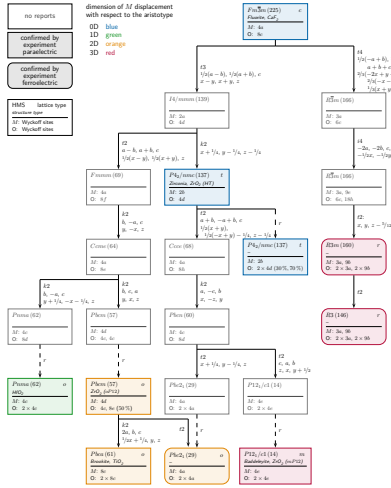
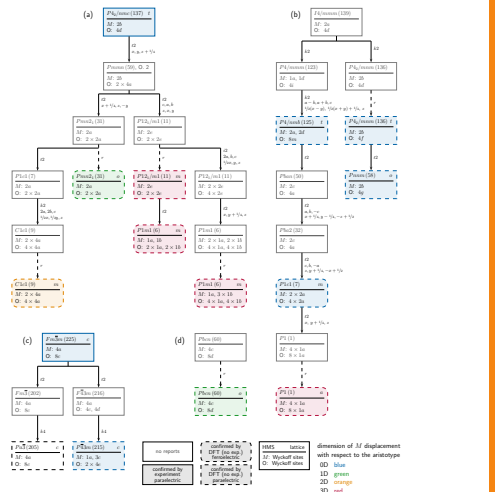
## Experimental Structure Types




## Theoretical Structure Types

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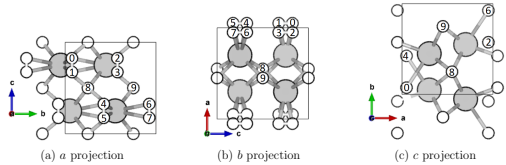
## Structure Comparison

- categorization by change in positional parameters
- first: displacements of Hf/Z
  second: O displacement and lattice parameter changes
- $(0,0,0) \rightarrow (x,x,x)$ is 1D displacement;
  $(0,0,0) \rightarrow (x,y,z)$ is 2D displacement
- group of 2D (3D) displaced Hf/Zr: strong structure relations!
  - $Pbcm\,(57)$
  - $Pbca\,(61)$
  - $Pbc2_1\,(29)$
  - $(P12_1/c1\,(14))$




(a) $a$ projection (b) $b$ projection (c) $c$ projection

- SG 57 is ordered variant of SG 61

| | *Pbca* (61) | | | | adaption SG 61 $2(x+1/4), y, z$ | | | *Pbcm* (57) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | site | $a/x$ | $b/y$ | $c/z$ | $a/x$ | $b/y$ | $c/z$ | site | $a/x$ | $b/y$ | $c/z$ | label |
| O | 8c | 0.98 | 0.74 | 0.49 | 0.46 | 0.74 | 0.49 | 4c | 0.46 | 3/4 | 1/2 | 9 |
| | | 0.52 | 0.26 | 0.99 | 0.54 | 0.26 | 0.99 | | 0.54 | 1/4 | 0 | 10 |
| | | 0.02 | 0.24 | 0.01 | 0.54 | 0.24 | 0.01 | | | | | 10 |
| | | 0.48 | 0.76 | 0.51 | 0.46 | 0.76 | 0.51 | | | | | 9 |
| | | 0.02 | 0.26 | 0.51 | 0.54 | 0.26 | 0.51 | | 0.54 | 1/4 | 1/2 | 8 |
| | | 0.48 | 0.74 | 0.01 | 0.46 | 0.74 | 0.01 | | 0.46 | 3/4 | 0 | 11 |
| | | 0.98 | 0.76 | 0.99 | 0.46 | 0.76 | 0.99 | | | | | 11 |
| | | 0.52 | 0.24 | 0.49 | 0.54 | 0.24 | 0.49 | | | | | 8 |

- SGs 29 and 14 are ordered variants of SG 57

| | *Pbcm* (57) | | | | | *Pbc2*$_1$ (29) | | | | *P*12$_1$1 (14) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | site | $a/x$ | $b/y$ | $c/z$ | label | site | $a/x$ | $b/y$ | $c/z$ | site | $a/x$ | $b/y$ | $c/z$ |
| O | 8e | 0.08 | 0.375 | 0.13 | 5 | 4a | 0.07 | 0.36 | 0.11 | 4e | | | |
| | | 0.92 | 0.625 | 0.63 | 3 | | 0.93 | 0.64 | 0.61 | | 0.93 | 0.67 | 0.65 |
| | | 0.92 | 0.875 | 0.37 | 6 | | | | | | | | |
| | | 0.08 | 0.125 | 0.87 | 0 | | | | | | 0.07 | 0.17 | 0.85 |
| | | 0.92 | 0.625 | 0.87 | 2 | | | | | | | | |
| | | 0.08 | 0.375 | 0.37 | 4 | | | | | | 0.07 | 0.33 | 0.35 |
| | | 0.08 | 0.125 | 0.63 | 1 | | 0.07 | 0.14 | 0.61 | | | | |
| | | 0.92 | 0.875 | 0.13 | 7 | | 0.93 | 0.86 | 0.11 | | 0.93 | 0.83 | 0.15 |

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## Application – Trace Reflections

- phase transition between phases $P_1$ to $P_2$
- What are the Miller indices of the reflection in $P_2$ corresponding to $hkl$ in $P_1$?
- find connection between P1 and P2 in Bärnighausen-like tree
- for each step: construct a matrix from coordinate transition (line-wise)
- multiply the matrices in the correct order for total transition matrix
- determine (dis)appearing reflections to study dynamics of phase transition

## Application – Example

- orthorhombic ($Pbc2_1, 29$) to tetragonal ($P4_2/nmc, 137$) phase with increasing temperature
- path is not unique, here via SG $Ccce\,(68)$
- coordinate transition from SG 137 to SG 68:

$$1/2(x+y), 1/2(-x+y), z \rightarrow \begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$M_{\text{total}} = M_{68\rightarrow 60} \cdot M_{137\rightarrow 68}$$

$$\begin{pmatrix} 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \\ -1/2 & 1/2 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- reflections $R$ of SGs 137 and 29:

$$R_{137} = M_{\text{total}}^{-1} \cdot R_{29}$$

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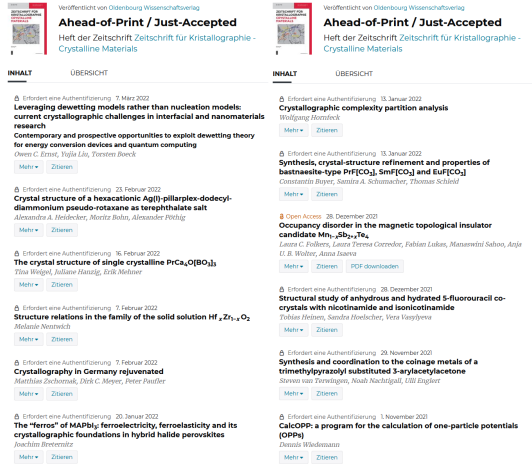
## Context

- published in the Special Issue *Spotlight on Germany's Young Crystallographers* of Zeitschrift für Kristallographie 2022
- Special Issue is from, by, and with the Young Crystallographers of the DGK
- `https://www.degruyter.com/journal/key/zkri/html`

## Some Contributions



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