IUCr participation to CODATA-VAMAS Working Group on the Description of Nanomaterials

D. Chateigner, J.R. Helliwell, R. Neder

CODATA-VAMAS WG: in Paris (ICSU): spring 2012, 2013, 2014

CODATA-VAMAS WG: Description of Nanomaterials

John Rumble, Steve Freiman, Clayton Teague

CODATA: Committee on Data for Science and Technology (www.codata.org)
VAMAS: Versailles Project on Advanced Materials and Standards (www.vamas.org)

- Creating a Framework for Uniform Description System for Materials on the Nanoscale: define a complete set of information categories of descriptors usable by all communities interested in nanomaterials
- Participants: ISO (TC229), Norway Ac Sci, OECD, IUPAC, IUCr, VAMAS, CODATA, ICSU, ARKEMA, ...
- Synthesis, formulation, properties, risks, production, purchase, legislation, regulation, standards, reference materials, databases …

IUCr contribution to this WG

Daniel Chateigner, John Helliwell, Reinhard Neder

Crystallography and related techniques provide physically sound information sets for nanomaterial descriptions:

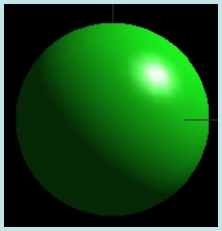
Structure, Microstructure and defects (0D to 3D), Phase content, Residual Stresses, Roughness, Thickness, Magnetism, Texture, Porosity …

Crystallography already developed a large open and adaptable nomenclature: CIF

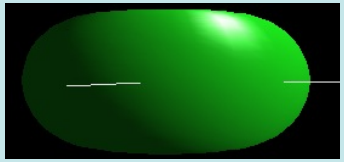
- CIF dictionaries (**existing** Core, Restraints, Powder, Modulated-Composite, Electron density, Twinning, Macromolecular, Images, Symmetry … **and to come** reflectivity, properties, MAUD …):
  Provide a formal taxonomy of terms and ideas, structured, machine-readable data
- databases: PDB, COD, NDB, AMCSD, Bilbao, IZA, crystal shapes, Raman, MPOD, TCOD, PCOD …
- data storage and preservation: Diffraction Data Deposition Working Group: http://forums.iucr.org/viewtopic.php?f=21&t=343

Microstructure, 3D to 0D, iso-anisotropic: size, distributions, twin faults, antiphase boundaries, stacking faults, turbostratism, intersticials, microdistortions …)

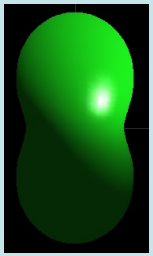
$\bar{1}$



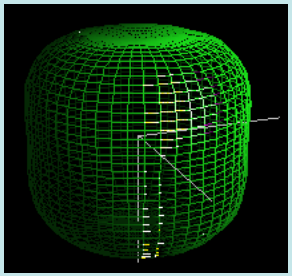
R_0



$R_0, R_1 < 0$



$R_0, R_1 > 0$

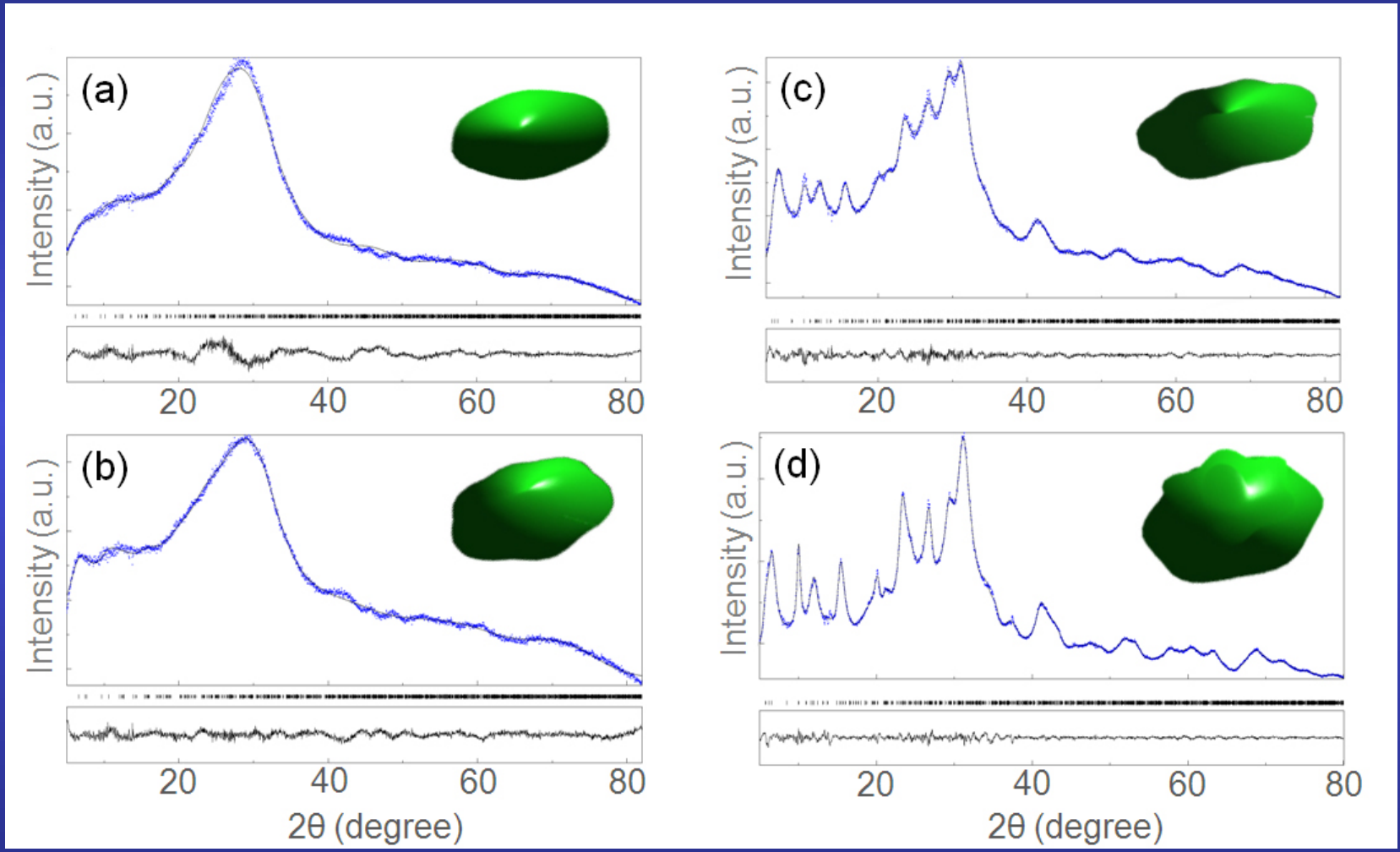


$R_0, R_6 < 0$

$$\langle R_{\mathbf{h}} \rangle = R_0 + R_1 P_2^{\,0}(x) + R_2 P_2^{\,1}(x)\cos\varphi + R_3 P_2^{\,1}(x)\sin\varphi + R_4 P_2^{\,2}(x)\cos 2\varphi + R_5 P_2^{\,2}(x)\sin 2\varphi +$$

$$\langle \varepsilon_{\mathbf{h}}^{\,2} \rangle E_{\mathbf{h}}^{\,4} = E_1 h^4 + E_2 k^4 + E_3 \ell^4 + 2E_4 h^2 k^2 + 2E_5 \ell^2 k^2 + 2E_6 h^2 \ell^2 + 4E_7 h^3 k + 4E_8 h^3 \ell + 4E_9 k^3 h + 4E_{10} k^3 \ell + 4E_{11} \ell^3 h + 4E_{12} \ell^3 k + 4E_{13} h^2 k \ell + 4E_{14} k^2 h \ell + 4E_{15} \ell^2 k h$$

EMT nanocrystalline zeolite



Ng, Chateigner, Valtchev, Mintova: *Science* **335** (2012) 70

```
#subordinateObject_Popa rules

_riet_sizestrain_sym_model 'Popa rules'

_rita_harmonic_expansion_degree 4

loop_
_riet_par_anisocryst_size
  3129.8965(67.47402)
  -339.8306(43.31268)
  455.05365(37.83163)
  1003.05383(27.05627)

loop_
_riet_par_aniso_microstrain
  2.627043E-4(2.0511094E-5)
  -3.466392E-5(3.9479637E-5)
  3.5241275E-5(5.5889054E-6)
  2.1924837E-4(4.90759E-6)


#end_subordinateObject_Popa rules
```

Crystallography probes down to nanoscale

From crystalline to amorphous states

Single crystals, Textured, Powders

Thin architectures and bulks

Structure
Microstructure
Phase content
Residual Stresses
Roughness
Thickness
Magnetism
Texture
Porosity

Crystallographic Techniques

Diffraction (scattering + interferences): X, γ, n, e^-

Reflectivity (specular, off-specular): x-rays and neutrons

Small-Angles Scattering: x-rays (SAXS), neutrons (SANS)

Tomography (absorption or phase contrasts): x-rays, neutrons, electrons

Spectroscopy: X (XRF, XANES, EXAFS, DAFS)
e^- (EDS)
μ^+ (μSR)

Crystallography Information File (CIF)

CIF dictionaries provide a formal taxonomy of crystallographic terms and ideas. Dictionary entries are constructed in a structured machine-readable manner that facilitates validation and structuring of data: http://www.iucr.org/resources/cif/dictionaries

Dictionaries: Core, Restraints, Powder, Modulated-Composite, Electron density, Twinning, Macromolecular, Images, Symmetry

Local dictionnaries: reflectivity (to come), MPOD (Properties), MAUD

Structure (unit-cell metric, atomic positions, thermal vibrations)

```
_cell_length_a 5.959(1)
_cell_length_b 14.956(1)
_cell_length_c 19.737(3)
_cell_angle_alpha 90
_cell_angle_beta 90
_cell_angle_gamma 90
_cell_volume 1759.0(3)
_cell_measurement_temperature 293
_cell_measurement_reflns_used 25
_cell_measurement_theta_min 25
_cell_measurement_theta_max 31
```

```
loop_
_atom_site_aniso_label
_atom_site_aniso_B_11
_atom_site_aniso_B_22
_atom_site_aniso_B_33
_atom_site_aniso_B_12
_atom_site_aniso_B_13
_atom_site_aniso_B_23
_atom_site_aniso_type_symbol
O1 .071(1) .076(1) .0342(9) .008(1) .0051(9) -.0030(9)
O
C2 .060(2) .072(2) .047(1) .002(2) .013(1) -.009(1) C
C3 .038(1) .060(2) .044(1) .007(1) .001(1) -.005(1) C
N4 .037(1) .048(1) .0325(9) .0025(9) .0011(9) -.0011(9)
N
C5 .043(1) .060(1) .032(1) .001(1) -.001(1) .001(1) C
# - - - - data truncated for brevity - - - -
O21 .094(2) .109(2) .068(1) .023(2) .038(1) -.010(1) O
C51 .048(2) .059(2) .049(1) .002(1) -.000(1) .007(1) C
C511 .048(2) .071(2) .097(3) -.008(2) -.003(2) .010(2) C
C512 .078(2) .083(2) .075(2) .009(2) -.005(2) .033(2) C
C513 .074(2) .055(2) .075(2) .004(2) .001(2) -.010(2) C
```

Tensor properties: c_{ij}, d_{ij}, π_{ijkl} …

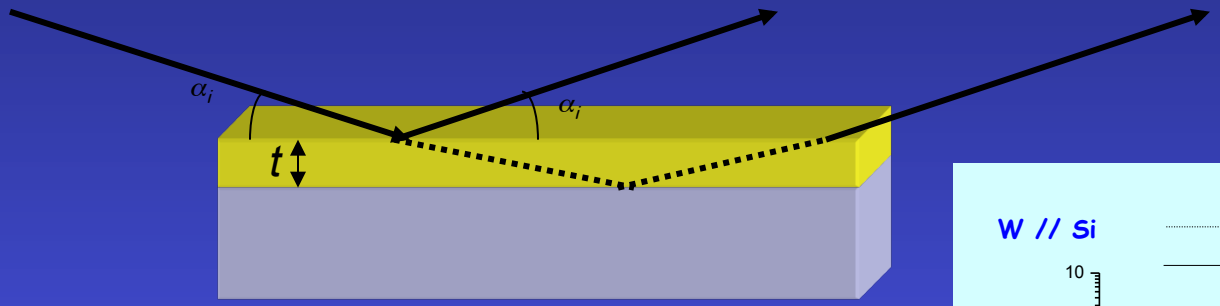
$$\begin{vmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ & & c_{33} & c_{34} & c_{35} & c_{36} \\ & & & c_{44} & c_{45} & c_{46} \\ & & & & c_{55} & c_{56} \\ & & & & & c_{66} \end{vmatrix}$$

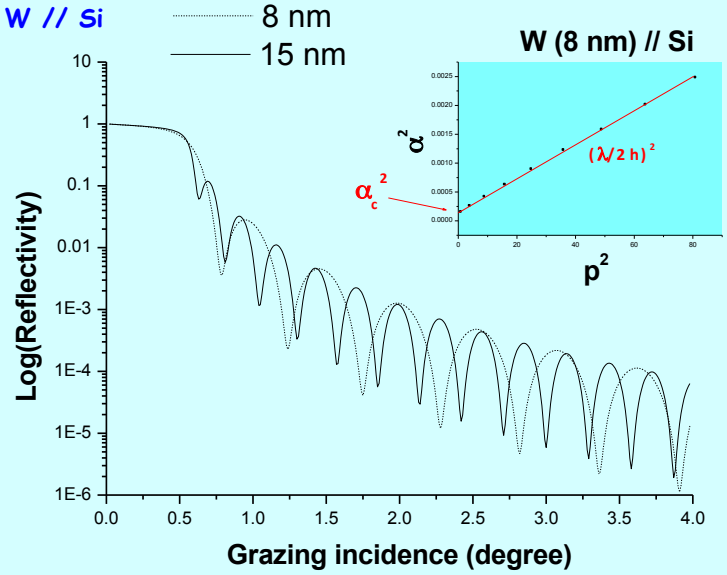
$$\begin{vmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{vmatrix}$$

```
_prop_elastic_stiffness_cij 'cij'
_prop_piezoelectric_dij 'dij'
_prop_conditions_temperature 257.0(5)

loop_
_prop_data_label
_prop_data_tensorial_index
_prop_data_value
_prop_measurement_method
cij 11 29.1(1) BS
cij 12 1.8(3) BS
cij 13 1.4(3) BS
cij 22 33.5(2) BS
cij 23 19.8(3) BS
cij 33 26.0(1) BS
cij 44 5.9(1) BS
cij 55 12.9(1) BS
cij 66 16.0(1)BS
dij 15 3100 RUS
dij 24 2435 RUS
dij 32 -302 RUS
dij 33 267 RUS
```

Specular Reflectivity



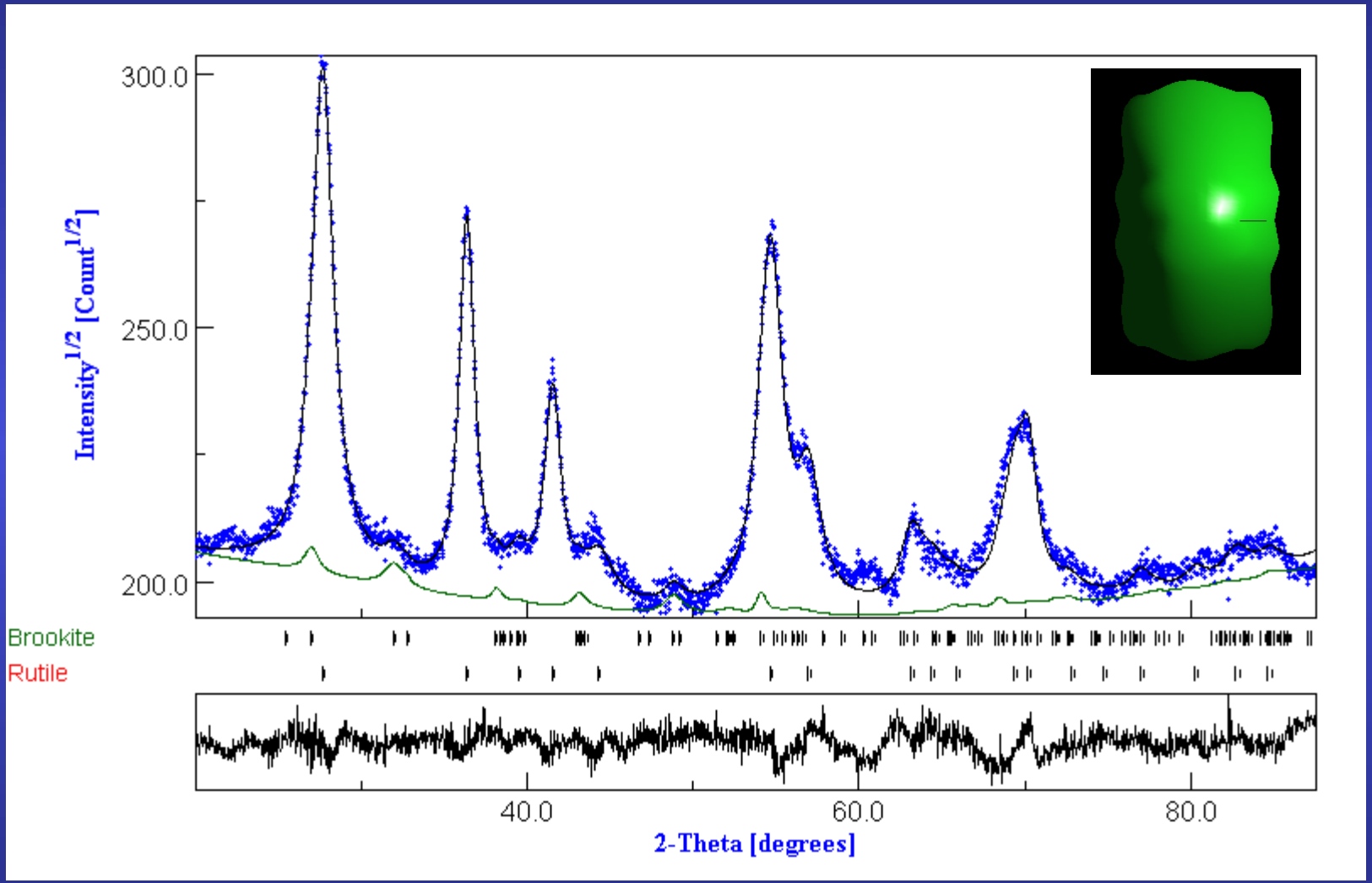


#subordinateObject_Layer_x1

_riet_spec_layer_id 'Layer_x1'
_riet_par_spec_layer_thickness 142.3256(1.5491493)
_reflectivity_layer_critical_qc 0.03169255(5.7467838E-5)
_reflectivity_layer_absorption 5.452058E-8(1.28723885E-8)
_reflectivity_layer_roughness 0.33851644(0.08996007)

#end_subordinateObject_Layer_x1

Phase Content



h	k	l	multiplicity	D-spacing	Crystallite	Microstrain
1	1	0	4	3.239971544546...	55.1405712350...	0.007826284017..
1	0	1	8	2.479909088830...	81.9223706294...	0.003242345868..
2	0	0	4	2.29100585	31.6754199507...	0.011068037
1	1	1	8	2.180965464211...	77.6940457026...	0.003546382641..
2	1	0	8	2.049137926979...	38.5103939859...	0.009126937123..
2	1	1	16	1.682810130360...	63.4940322756...	0.006155376929..
2	2	0	4	1.619985772273...	55.1405712350...	0.007826284017..
0	0	2	2	1.4745978	38.2388623632...	5.354081304805..
3	1	0	8	1.448959323754...	31.9401516263...	0.010022533775..
2	2	1	8	1.419878292695...	44.9379786288...	0.006012240827..
3	0	1	8	1.356252797441...	80.5993482184...	0.008727349807..

```
_riet_spec_layer_id 'layer1'

_riet_par_spec_layer_thickness 1.0E8

loop_
_pd_phase_atom_%
  0.9201359(0.004872608)
  0.07986411(0.0069217416)

#end_subordinateObject_layer1
```

Free and Fee Databases and Tools: use CIF intensively !

COD (crystal structures): www.crystallography.net
PCOD (predicted crystal structures): www.crystallography.net/pcod
TCOD (theoretical crystal structures): www.crystallography.net/tcod
MPOD (properties): www.materialproperties.org
PDB (proteins): http://www.wwpdb.org
NDB (nucleic acids): http://ndbserver.rutgers.edu/
AMCSD (minerals): http://rruff.geo.arizona.edu/AMS/amcsd.php
IZA (zeolites): http://www.iza-structure.org/databases
Raman (minerals): http://minerals.gps.caltech.edu/files/raman
Bilbao Server (aperiodic): http://www.cryst.ehu.es
Crystal-Eye (merged 2014): http://wwmm.ch.cam.ac.uk/crystaleye/
PubChem
AtomWork
FPSM (Full-Pattern Search-Match): http://cod.iutcaen.unicaen.fr

CSD, ICSD, CrystMet, PDF, Pauling, Pearson
Highscore (Panalytical), Eva (Bruker), Search-Match (Crystal Impact),
PDXL (Rigaku), 3DSystems, PolyXtal (Jordan Valley Semiconductors)