



Crystallization Techniques and Materials for Double Beta Decay Studies

I. Dafinei

INFN Sezione di Roma, ITALY



- introduction
- crystal growth
 - nucleation and growth
 - crystal growth methods
 - crystal growth from the melt
- crystals for Double Beta Decay (DBD)
 - DBD application constraints
 - TeO_2 "case study"

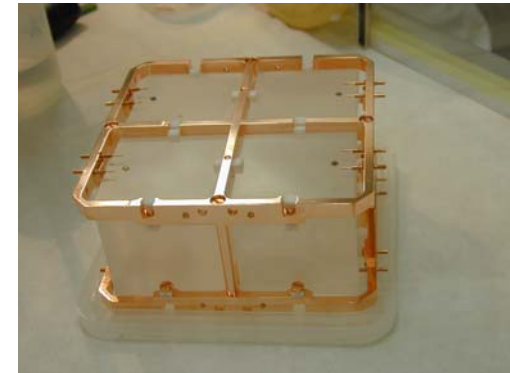


low temperature detectors (LTD)

very good energy resolution ($<0.01\text{eV}$)
 very low energy threshold
 sensitivity to non-ionizing events

**practically unlimited
 choice for energy
 absorber**

$$\Delta T = \frac{\varepsilon}{C} \quad C \propto \left(\frac{T}{\Theta_D} \right)^3$$



CUORICINO/CUORE
 4 x 760 g detectors

**material (radio)purity is the major limitation of
 LTD use in Rare Events Physics applications**

$$\Lambda_{\beta\beta\text{TeO}_2} \approx 30 \mu\text{Bq} / \text{kg}$$



material synthesis

detector construction



why crystal growth ?

• research



properties of solids may be obscured by grain boundaries

- metals
- insulators
- semiconductors
- superconductors
- protein crystals
- ...

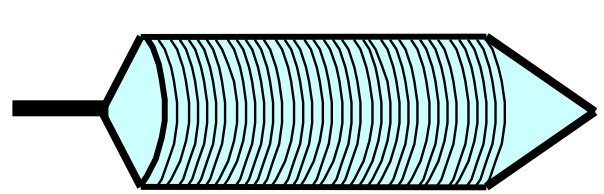
• applications



uniform properties on microscopic level

micro-devices

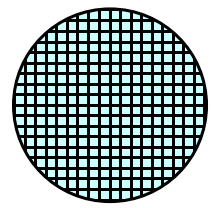
- electronics
- optics
- mechanics



1 boule



~1 wafer/mm



~ 10⁶
devices



very high stability in time

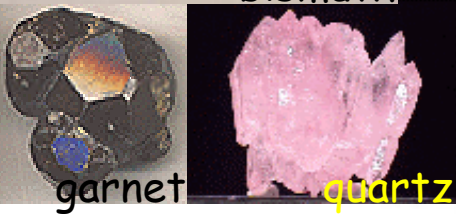


beautiful

nucleation and growth



bismuth



garnet

quartz

$$k = k_0 \cdot e^{-E/k_B \cdot T}$$

$$k = \frac{k_B \cdot T}{h} \cdot e^{\Delta S^*/k_B} \cdot e^{\Delta H^*/k_B \cdot T}$$

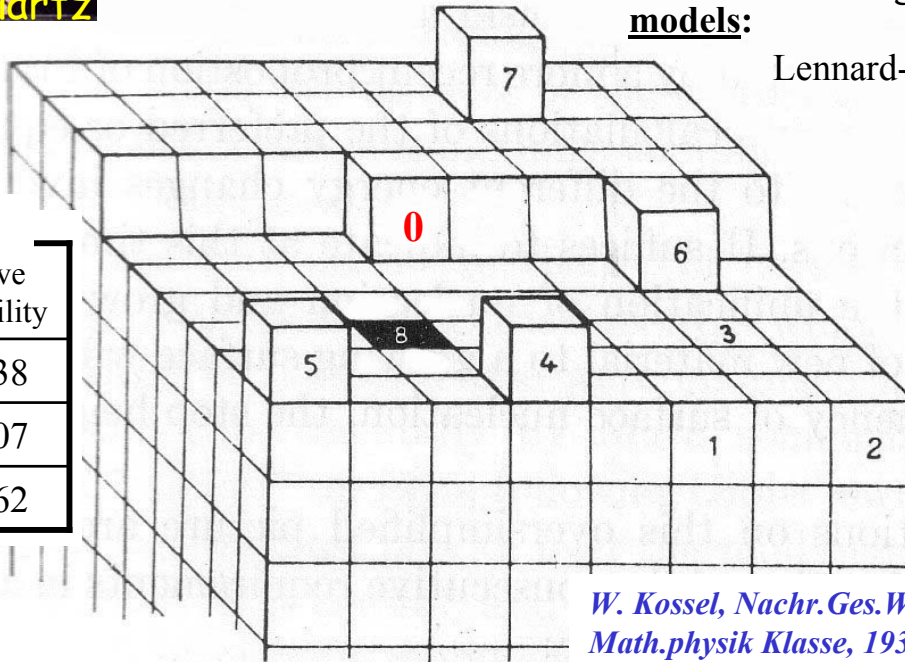
Kossel: growth from vapour and from solution

Lennard-Jones: growth from a melt

models:

in the case of NaCl

position	relative probability
0	0.8738
1	0.1807
2	0.0662



$$\Phi_{L-J}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

$$V(r_1, \dots, r_N) = \sum_i \sum_{j>i} \Phi_{L-J}(|r_i - r_j|)$$

W. Kossel, Nachr. Ges. Wiss. Gottingen, Math. physik Klasse, 1935 (1927), Ann. Physik., 21, 455 (1934) ; 33, 651 (1938)

present:

Monte Carlo modeling of reactions on the surface of the growing crystal



quartz



generally classified as:

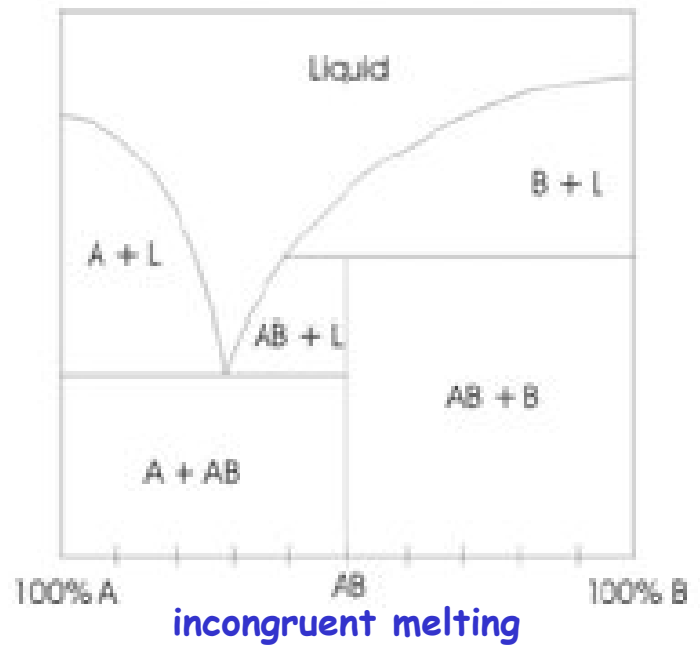
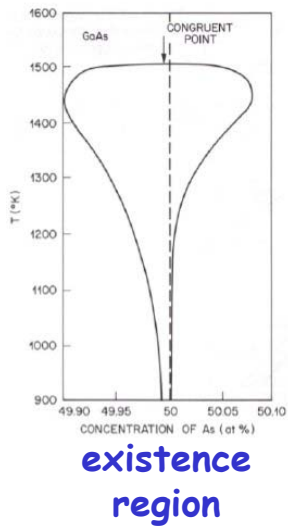
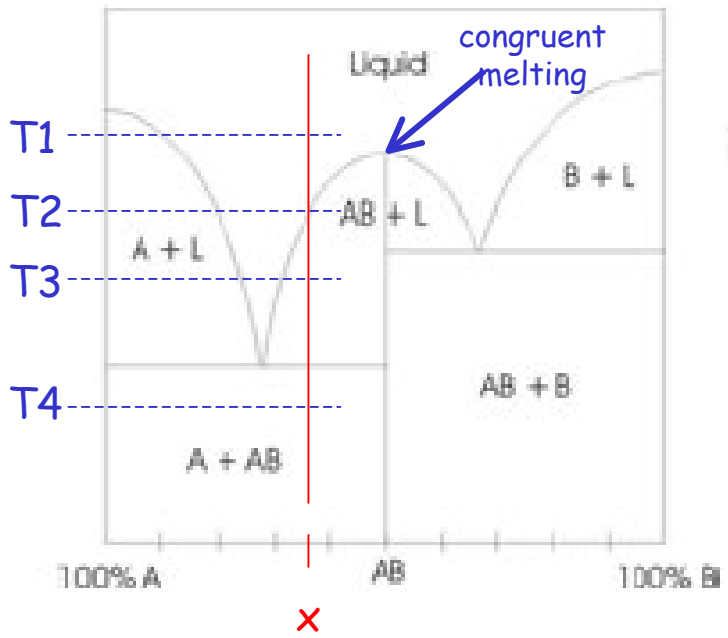
each method has several different versions 😊

- melt growth directional solidification from the melt ~ mm/hr
- solution growth supersaturation ~ mm/day
- vapor growth sublimation-condensation ~ $\mu\text{m/hr}$



feasibility conditions:

- congruent melting
 - not trivial in the case of binary or more compounds





feasibility conditions (continued):

- raw material must not decompose before melting
 - changes in stoichiometry of the melt due to different evaporation rates are also to be avoided
- grown crystal must not undergo a solid state phase transformation when cooled down to room temperature

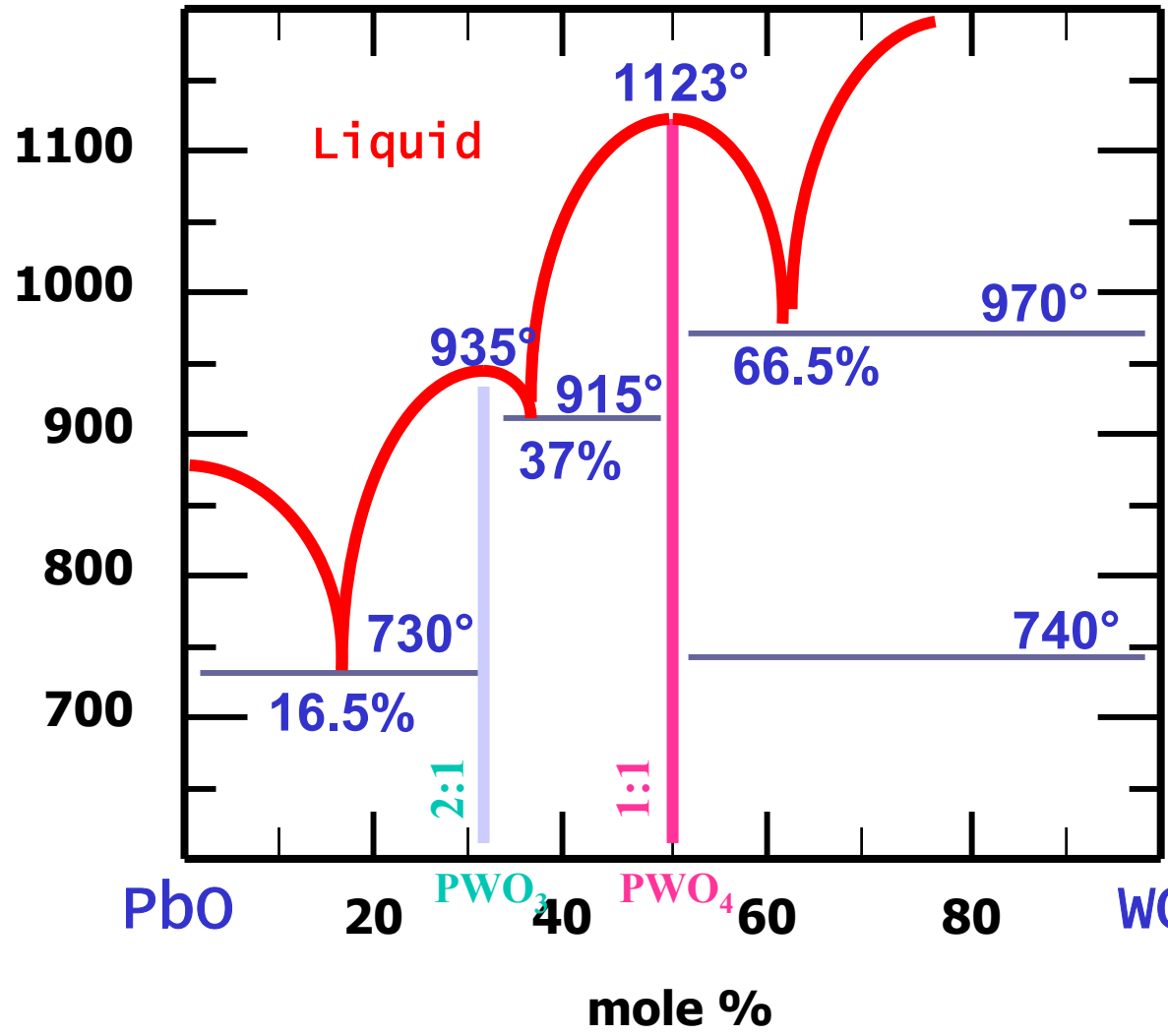
preliminary detailed study
of phase diagram is needed

- thermodifferential analysis
- thermogravimetical analysis
- X-ray diffraction analysis
- ...



example

PbO-WO₃
compounds



Chang, 1971

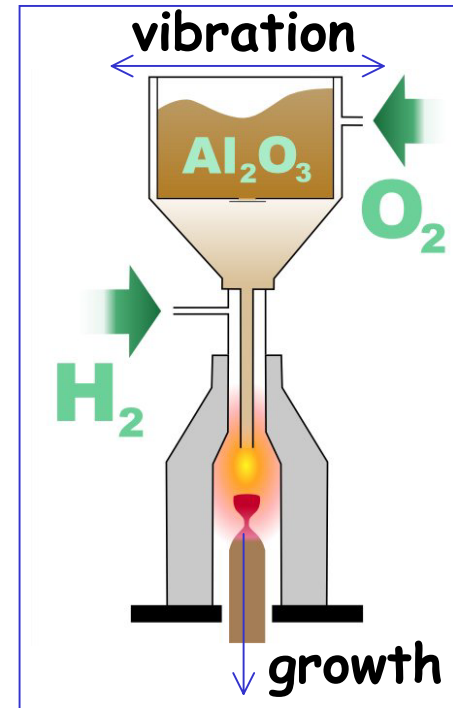
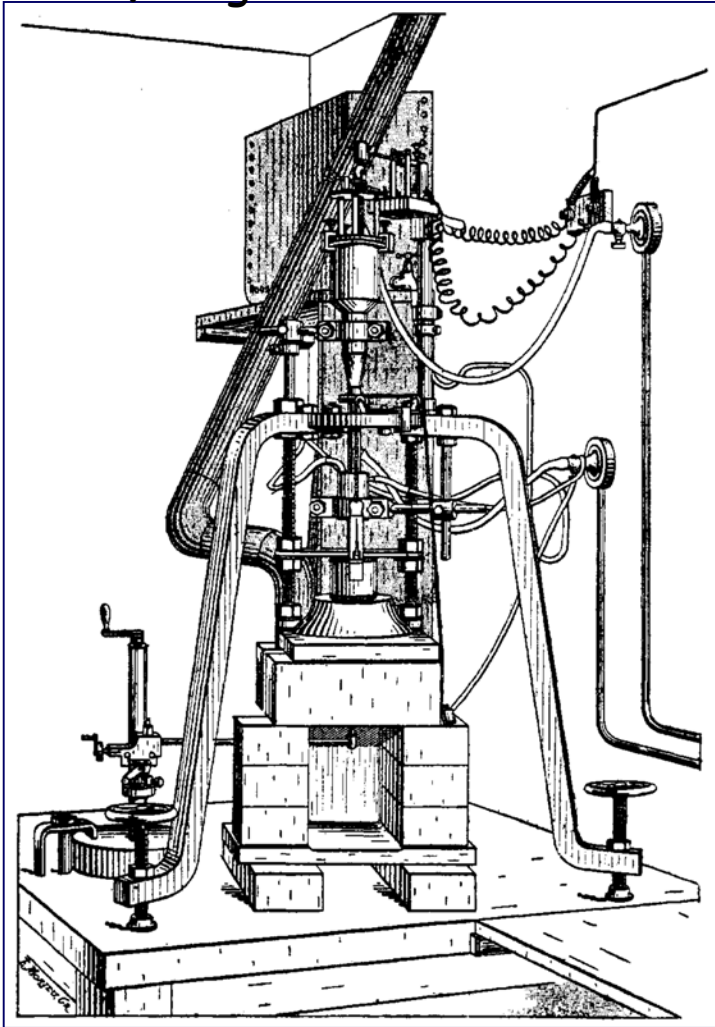
growth from the melt (4) characteristics



- fast (\sim mm/hr) growth rate is limited by heat transfer, not by mass transfer
- allows for a large variety of techniques
 - Verneuil
 - Bridgman-Stockbarger
 - Czochralski-Kyropoulos
 - zone melting and floating zone



1902, Auguste Verneuil

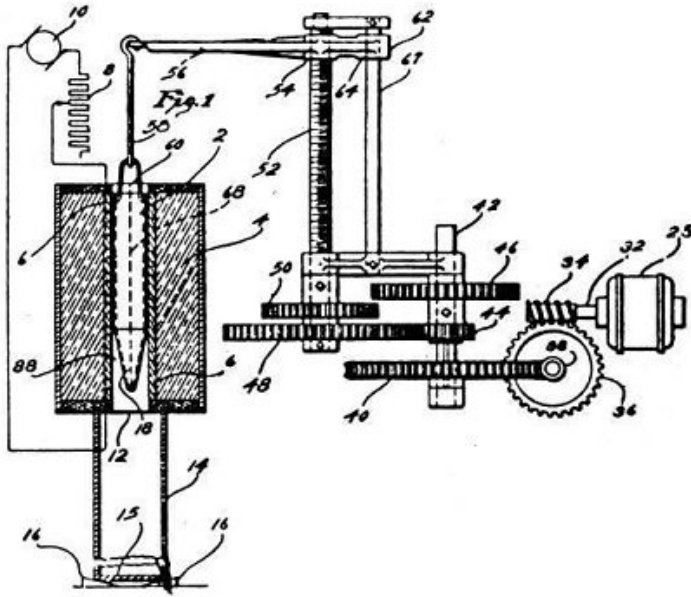


characteristics:

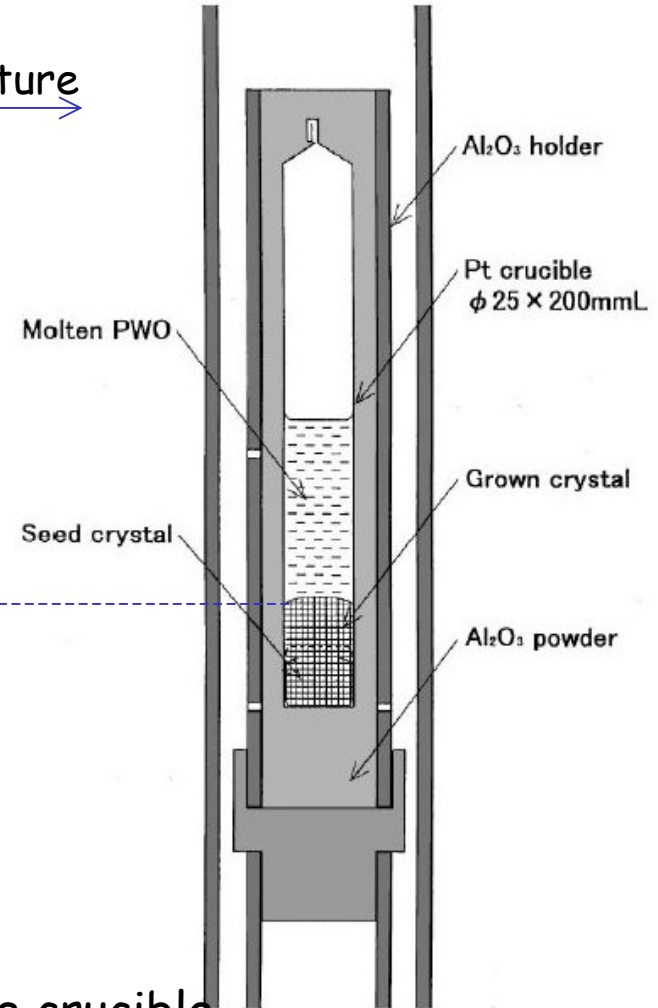
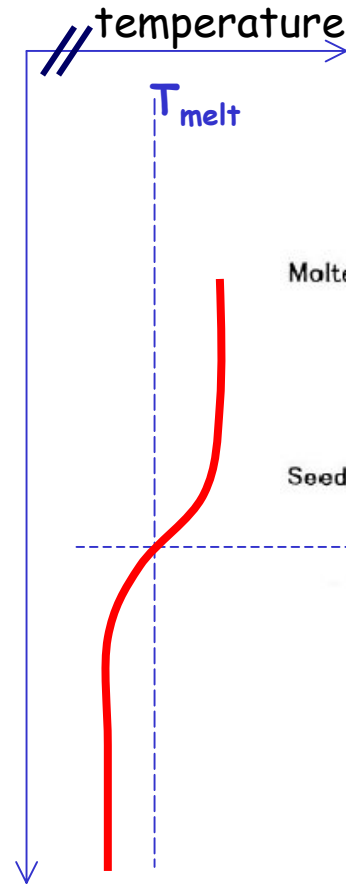
- no crucible contamination
- highly pure starting material (>99.9995%)
- strict control of flame temperature
- precise positioning of melted region



1,793,672. CRYSTALS AND THEIR MANUFACTURE.
PERCY W. BRIDGMAN, Cambridge, Mass. Filed Feb. 16,
1926. Serial No. 88,650. 41 Claims. (Cl. 22—212.)



1. A method of solidifying a molten substance that comprises placing a seed crystal adjacent to the substance, melting a portion of the seed crystal adjacent to the substance, and advancing the surface of solidification from the seed crystal into the substance.



characteristics:

- charge and seed are placed into the crucible
- no material is added or removed (conservative process)
- axial temperature gradient along the crucible



advantages

- the shape of the crystal is defined by the container
- no radial temperature gradients are needed to control the crystal shape.
- low thermal stresses result in low level of stress-induced dislocations.
- crystals may be grown in sealed ampules (easy control of stoichiometry)
- relatively low level of natural convection
- easy control and maintenance

drawbacks

- confined growth (crucible may induce stresses during cooling)
- difficult to observe seeding and growing processes
- changes in natural convection as the melt is depleted
- delicate crucible and seed preparation, sealing, etc.



applications

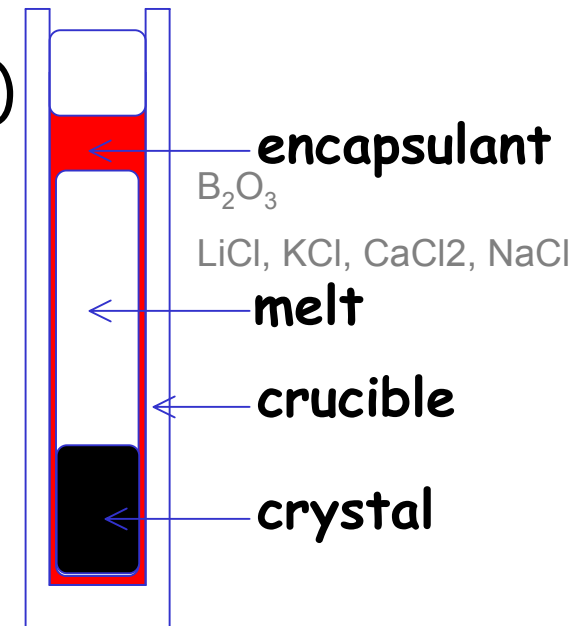
- melts with volatile constituents:
 - III-V compounds ($GaAs$, InP , $GaSb$)
 - II-VI compounds ($CdTe$)
- ternary compounds:
 - $Ga_{1-x}In_xAs$, $Ga_{1-x}In_xSb$, $Hg_{1-x}Cd_xTe$

improvement example (liquid encapsulation)

- reduced nucleation
- reduced thermal stresses
- reduced evaporation
- prevents contact between crucible and melt

encapsulant characteristics

- low vapor pressure
- melting temperature lower than the crystal
- density lower than the density of the melt
- no reaction with the melt or crucible

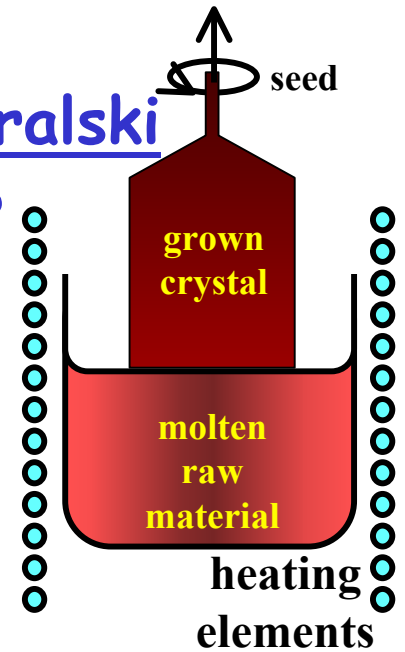




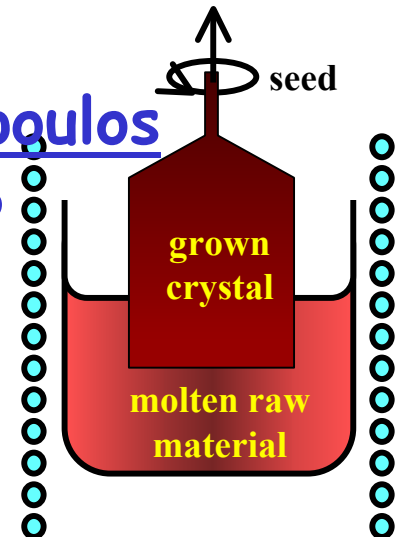
Jan Czochralski
(1885 - 1953)

A seed crystal mounted on a rod is dipped into the molten material. The seed crystal's rod is pulled upwards and rotated at the same time. By precisely controlling the temperature gradients, rate of pulling and speed of rotation, a single-crystal cylindrical ingot is extracted from the melt. The process may be performed in controlled atmosphere and in inert chamber.

Czochralski
1918



Kyropoulos
1926



characteristics:

- charge and seed are separated at start
- no material is added or removed
(conservative process)
- charge is held at temperature slightly above melting point
- crystal grows as atoms from the melt adhere to the seed

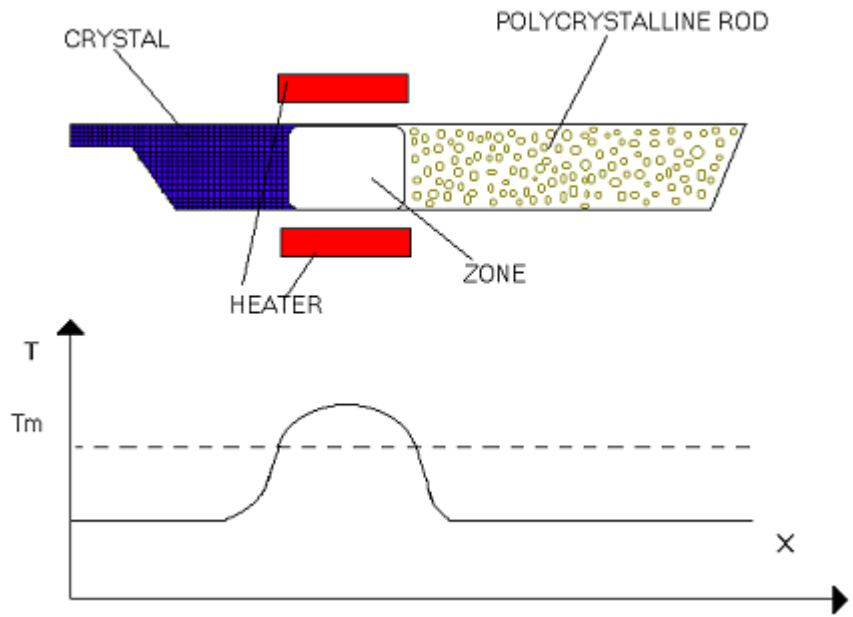


advantages

- growth from free surface (stress free)
- crystal can be observed during the growth process
- forced convection easy to impose
- large crystals can be obtained
- high crystalline perfection can be achieved
- good radial homogeneity

drawbacks

- delicate start (seeding, necking) and sophisticated further control
- delicate mechanics (the crystal has to be rotated; rotation of the crucible is desirable)
- cannot grow materials with high vapor pressure
- batch process (axial segregation, limited productivity)



characteristics:

- only a small part of the charge is molten
- material is added to molten region (nonconservative process)
- molten zone is advanced by moving the charge or the gradient
- axial temperature gradient is imposed along the crucible



advantages

Charge is purified by repeated passage of the zone (zone refining).

Crystals may be grown in sealed ampules or without containers (floating zone).

Steady-state growth possible.

Zone leveling is possible; can lead to superior axial homogeneity.

Process requires little attention (maintenance).

Simple: no need to control the shape of the crystal.

Radial temperature gradients are high.

drawbacks

Confined growth (except in floating zone).

Hard to observe the seeding process and the growing crystal.

Forced convection is hard to impose (except in floating zone).

In floating zone, materials with high vapor pressure can not be grown.



growth from solutions

- melt non congruently
- decompose before melting
- have very high melting point
- undergo solid state phase transformation between melting point and room temperature

key requirement

high purity solvent
insoluble in the crystal

molten salt (flux) growth

- oxides with very high melting points



typical solvents: PbO , PbF_2 , B_2O_3 , KF

main advantage: carried on at much lower temperature than melting point

limitations: very slow, borderline purity, platinum crucibles, stoichiometry hard to control

flux:

a liquid reaction medium that dissolves the reactants and products, but do not participate in the reaction



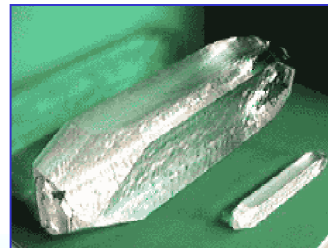
liquid phase epitaxy

- high quality layers of III-V compounds ($\text{Ga}_{1-x}\text{In}_x\text{As}$, $\text{GaAs}_x\text{P}_{1-x}$)
- GaAs and GaSb from Ga solution

hydrothermal growth

- aqueous solution at high temperature and pressure
- typical example: quartz industry

SiO_2 is grown by hydrothermal growth at 2000 bars and 400°C because of α - β quartz transition at 583°C

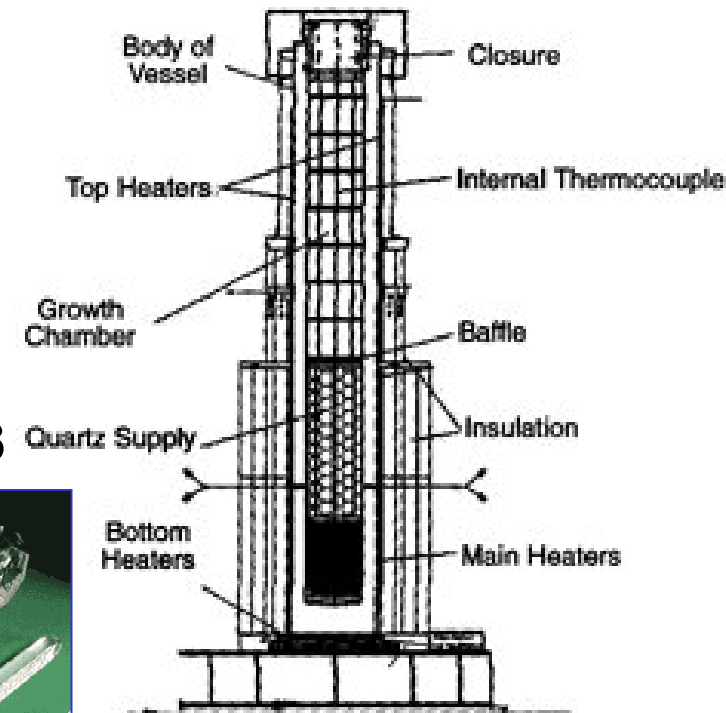


advantage

lower temperatures than melt growth

limitation

very slow, small crystals or thin layers





Solubility of possible impurity is different in crystal than melt, the ratio between respective concentrations is defined as segregation coefficient (k_0)

$$k_0 = \frac{C_S}{C_L}$$

← impurity equilibrium concentration in crystal
 ← impurity equilibrium concentration in melt

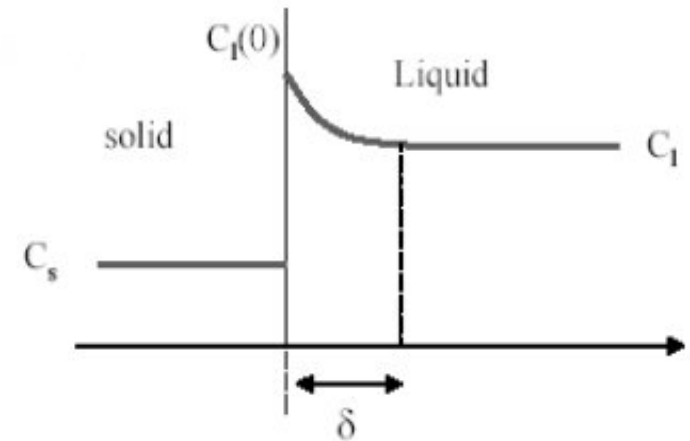
As the crystal is pulled impurity concentration will change in the melt (becomes larger if segregation coefficient is <1). Impurity concentration in crystal after solidifying a weight fraction M/M_0 is:

$$C_S = k_0 \cdot C_{L_0} \cdot \left(1 - \frac{M}{M_0}\right)^{k_0 - 1}$$



The effective segregation coefficient (k_e):

$$k_e = \frac{k_0}{k_0 + (1 - k_0) \cdot e^{-\frac{v \cdot \delta}{D}}}$$



As a consequence, floating zone method will give crystals with lower concentration of impurities having $k < 1$ than Czochralski growth

$$C_s = C_0 \cdot \left[1 - (1 - k_e) \cdot e^{-\frac{k_e \cdot x}{L}} \right]$$

- ◆ multiple pass may be run in order to achieve the required impurity concentration
- ◆ there is no contamination from crucible



DBD application constraints

$\beta\beta$ emitters of experimental interest

Isotope	Isotopic abundance (%)	half life (y)
^{48}Ca	0.0035	10^{19}
^{76}Ge	7.8	10^{21}
^{82}Se	9.2	10^{20}
^{96}Zr	2.8	10^{19}
^{100}Mo	9.6	10^{18}
^{116}Cd	7.5	10^{19}
^{128}Te	31.7	10^{24}
^{130}Te	34.5	10^{21}
^{136}Xe	8.9	?
^{150}Nd	5.6	10^{18}

$$\frac{\Lambda_i}{\Lambda} = \frac{p_i}{p} \cdot \frac{\mu}{\mu_i} \cdot \frac{m_i}{m} \cdot \frac{T}{T_i} \approx \frac{m_i}{m} \cdot \frac{T}{T_i}$$

impurity allowed (g/g):

$$\frac{m_i}{m} \ll \frac{T_i}{T}$$

$$T = 10^{18} - 10^{24} \text{ yr}$$

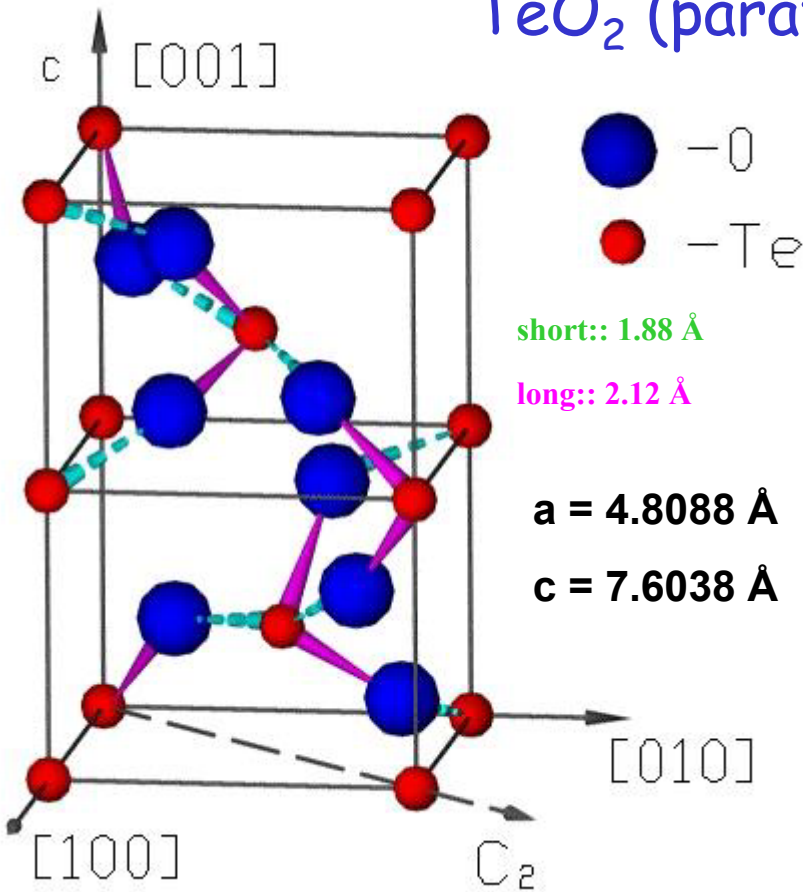
usual $T_i < 10^{12} \text{ yr}$

$$\frac{m_i}{m} < 10^{-12}$$

close to detection limit of the most sensitive techniques used for quantitative elemental analysis (NAA, ICP-MS)



TeO₂ (paratellurite)



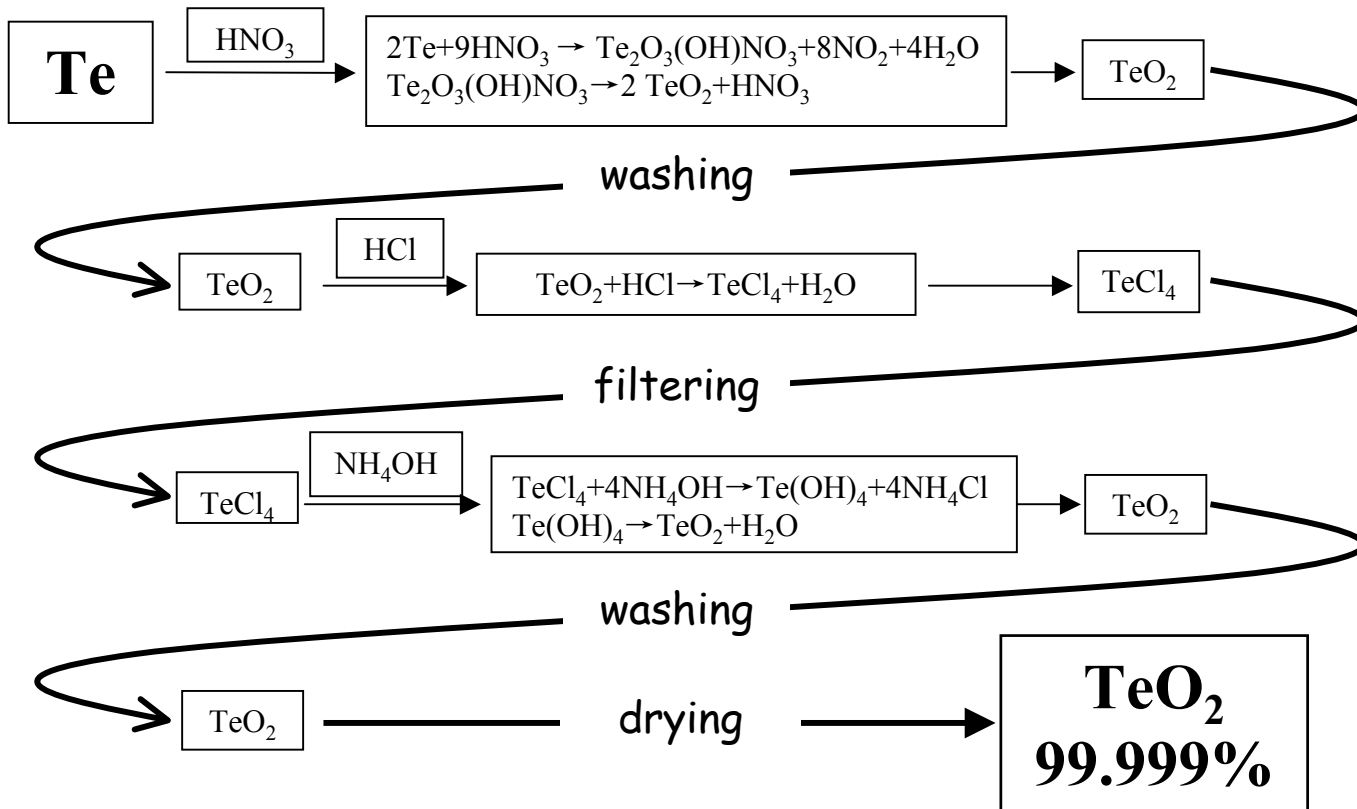
Characteristic	value
Chemical Formula	TeO ₂
Molecular Weight	159.61
Crystal Class	Tetragonal
Density (g/cm ³ at 20 °C)	6
Melting Point (°C)	733°C
Hardness (Mohs)	4
Solubility in water	None
Color	Clear
Transmittance Range (μm)	0.33-5.0
Refractive index (λ=500nm)	n _o =2.3194
	n _e =2.4829
Thermal Expansion (1/K at 0°C)	
normal to <001>	19.5 x 10 ⁻⁶
parallel to <001>	6.10 x 10 ⁻⁶

Paratellurite	Tellurite
tetragonal	orthorhombic-dipyramidal
greyish-white, opaque	white to yellow, subtranslucent to opaque
1960, Mexico	1842, Romania

- relatively low melting point
- distorted rutile (TiO₂) structure
- anisotropy of expansion coefficient

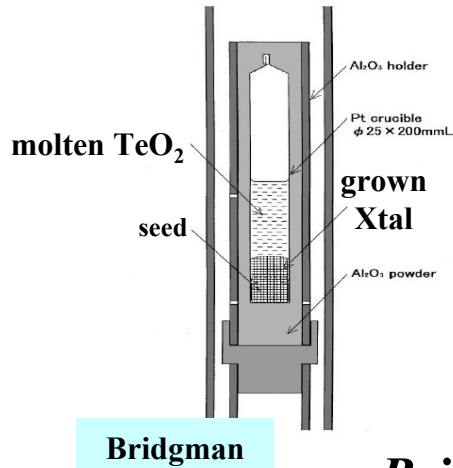
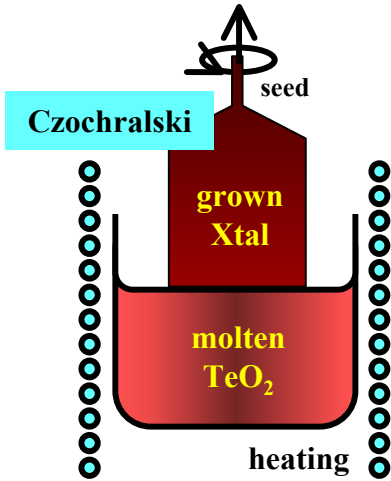


raw material preparation





crystal growth



- TeO₂ crystal is particularly repellent to impurities
- most of radioactive isotopes have ionic characteristics incompatible with substitutional incorporation in TeO₂

- *Bridgman grown crystals are more stressed than Czochralski ones*
- *annealing at about 550°C helps in removing the residual stresses*



Te possible substitutional ions in TeO₂

At	At. Nb.	Oxi. No.	Coo. No.	IonicR (Å)	Stable isot. (%)	Dev. IonR (%)
Ag	47	3	4	0.67	100.000	1.52
Au	79	3	4	0.68	100.000	3.03
Co	27	2; 2	6; 5	0.65; 0.67	100.000	-1.52; 1.52
Fe	26	2; 3	4; 6	0.64; 0.65	100.000	-3.03; -2.27
Ir	77	3	6	0.68	100.000	3.03
Mg	12	2	5	0.66	100.000	0
Mn	25	2; 2; 3	6; 4; 6	0.66; 0.67; 0.65	100.000	0; 1.52; -2.27
Mo	42	4; 5	6; 4	0.65; 0.65	75.530	-1.52; -1.52
Nb	41	4; 5	6; 6	0.68; 0.64	100.000	3.03
Pb	82	2; 4	4; 4	0.64; 0.65	98.600	-3.03; -1.52
Pd	46	2	4	0.64	100.000	-3.03
Rh	45	3	6	0.665	100.000	0.76
Ru	44	3	6	0.68	100.000	3.03
Ta	73	4; 5	6	0.68; 0.64	99.988	3.03; -3.03
Te	52	4	4	0.66	33.606	0
Ti	22	3	6	0.67	100.000	1.51
V	23	3	6	0.64	99.750	-3.03
W	74	4	6	0.66	55.440	0
Zr	40	4	5	0.66	97.200	0

Symbol	Approximate Detection Limit		
	NAA (ng)	XRF (µg/g)	ICP-MS (pg/g)
Cs	0.1	5	0.1
Co	0.1	1	3
Pb	--	1	10
Mo	1	0.5	2
Pd	1	5	0.1
K	1	10	200
Ra	0.1	5	1
Ta	0.1	2	0.01
Th	0.1	1	0.01
W	0.01	1	1
U	0.01	1	0.3
V	0.1	1	1
Zr	10	0.5	1

$${}^{238}\text{U} (T=4.5 \cdot 10^9 \text{ yr}) \quad \frac{T_i}{T} \approx 10^{-12}$$

$${}^{184}\text{W} (T=3 \cdot 10^{17} \text{ yr}) \quad \frac{T_i}{T} \approx 10^{-4}$$



radiopurity

Periodic Table of Elements

Groups

Periods	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA			IB	IIB	IIIB	IVB	VB	VIB	VIIA	VIIIA
	IA	IIA	IIIB	IVB	VB	VIB	VIIA	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	<u>1</u> H																	<u>2</u> He
2	<u>3</u> Li	<u>4</u> Be									<u>5</u> B	<u>6</u> C	<u>7</u> N	<u>8</u> O	<u>9</u> F	<u>10</u> Ne		
3	<u>11</u> Na	<u>12</u> Mg									<u>13</u> Al	<u>14</u> Si	<u>15</u> P	<u>16</u> S	<u>17</u> Cl	<u>18</u> Ar		
4	<u>19</u> K	<u>20</u> Ca	<u>21</u> Sc	<u>22</u> Ti	<u>23</u> V	<u>24</u> Cr	<u>25</u> Mn	<u>26</u> Fe	<u>27</u> Co	<u>28</u> Ni	<u>29</u> Cu	<u>30</u> Zn	<u>31</u> Ga	<u>32</u> Ge	<u>33</u> As	<u>34</u> Se	<u>35</u> Br	<u>36</u> Kr
5	<u>37</u> Rb	<u>38</u> Sr	<u>39</u> Y	<u>40</u> Zr	<u>41</u> Nb	<u>42</u> Mo	<u>43</u> Tc	<u>44</u> Ru	<u>45</u> Rh	<u>46</u> Pd	<u>47</u> Ag	<u>48</u> Cd	<u>49</u> In	<u>50</u> Sn	<u>51</u> Sb	<u>52</u> Te	<u>53</u> I	<u>54</u> Xe
6	<u>55</u> Cs	<u>56</u> Ba	<u>57</u> La	<u>72</u> Hf	<u>73</u> Ta	<u>74</u> W	<u>75</u> Re	<u>76</u> Os	<u>77</u> Ir	<u>78</u> Pt	<u>79</u> Au	<u>80</u> Hg	<u>81</u> Tl	<u>82</u> Pb	<u>83</u> Bi	<u>84</u> Po	<u>85</u> At	<u>86</u> Rn
7	<u>87</u> Fr	<u>88</u> Ra	<u>89</u> Ac	<u>104</u> Rf	<u>105</u> Db	<u>106</u> Sg	<u>107</u> Bh	<u>108</u> Hs	<u>109</u> Mt	<u>110</u> Uun	<u>111</u> Uuu	<u>112</u> Uub		<u>114</u> Uuq		<u>116</u> Uuh		<u>118</u> Uuo
6			<u>58</u> Ce	<u>59</u> Pr	<u>60</u> Nd	<u>61</u> Pm	<u>62</u> Sm	<u>63</u> Eu	<u>64</u> Gd	<u>65</u> Tb	<u>66</u> Dy	<u>67</u> Ho	<u>68</u> Er	<u>69</u> Tm	<u>70</u> Yb			
7			<u>90</u> Th	<u>91</u> Pa	<u>92</u> U	<u>93</u> Np	<u>94</u> Pu	<u>95</u> Am	<u>96</u> Cm	<u>97</u> Bk	<u>98</u> Cf	<u>99</u> Es	<u>100</u> Fm	<u>101</u> Md	<u>102</u> No			

Annotations on the periodic table:

- natural radioactivity (underlined in red)
- activation products (underlined in red)
- crucible material (underlined in red)
- Red circles around elements: K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Rf, Db, Sg, Bh, Hs, Mt, Uun, Uuu, Uub, Uuq, Uuh, Uuo, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No.
- Blue circle around Te.
- Yellow circles around K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Rf, Db, Sg, Bh, Hs, Mt, Uun, Uuu, Uub, Uuq, Uuh, Uuo, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No.

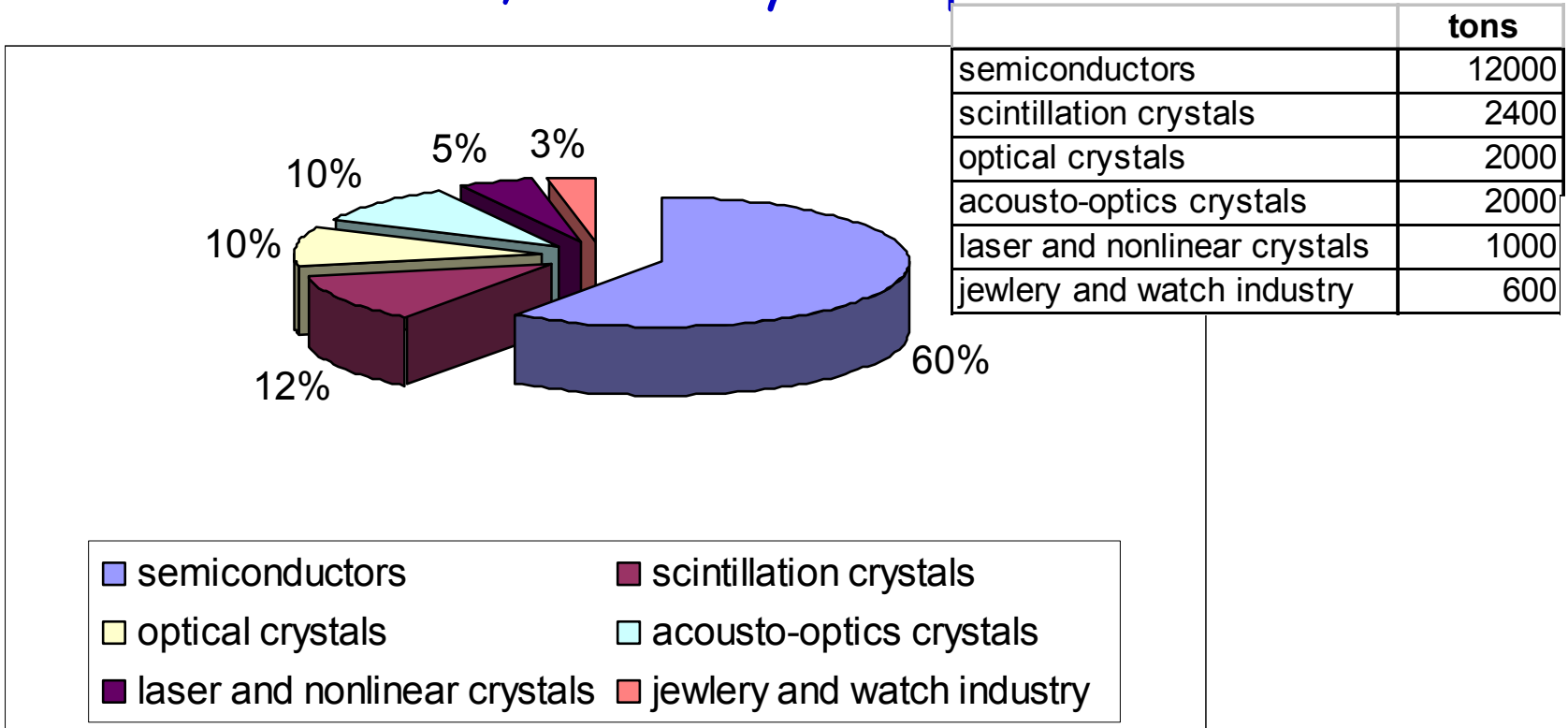
	ox. No.	coo. No.	ion rad. (Å)
Te	4	4	0.66
Co	3	6	0.61
Pa	4	6	0.90
Th	4	6	0.94
U	4	6	0.89
V	3	6	0.64
	4	5	0.53
Pt	4	6	0.58
	3	6	0.70
	4	6	0.70

	decay mode	energy (MeV)	T1/2
⁴⁰ K	beta	1.311	1.277E11 y
¹⁹⁰ Pt	alpha	3.249	6.5E11 y
⁵⁰ V	e ⁻ capture	2.208	1.4E17 y
	beta	1.037	1.4E17 y

main radioactive series



shares of 20 000 tons, world crystals production in 1999



ECAL-CMS: (≈ 80 tons PWO)/2000-2006

CUORE: (≈ 1 ton TeO_2)/?