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# School and Workshop on Highly Frustrated Magnets and Strongly Correlated Systems: From Non-Perturbative Approaches to Experiments

***30 July - 17 August, 2007***

## II. Materials preparation and crystal growth

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# II. Materials preparation and crystal growth.

## A. Control of transition metal oxidation state and oxygen stoichiometry.

1. Oxygen affinity, pO, buffer gases

## B. Crystal growth methods.

1. Bridgeman
2. Czochralski
3. Floating zone
4. Flux
5. Hydrothermal

## C. “Soft chemical” routes to metastable phases

## Oxygen affinity of metals.

- to assess the relative stability of the oxides of metals or the ability of metals to bind oxygen.

- recall, (from undergraduate physical chemistry)

“ formation reaction ”

$$M_{(s)} + O_{2(g)} = MO_{2(s)}$$

$$MO_{2(s)} = M_{(s)} + O_{2(g)}$$

“dissociation”

(s) = solid
(g) = gas

- **equilibrium constant at T:**

**(for dissociation)**

$$K_T = pO_2$$

$$\Delta G_0 = -RT\ln K_T$$

**$\Delta G_0$ - Gibbs energy, $\Delta G_0 = \Delta H_0 - T\Delta S_0$**

**define: $pO = -\log pO_2$**

**and $pO = -\Delta G_0/2.303RT$**

**a useful T = 1000K,**

**$\therefore\ pO = -\Delta G_0/(2.303R)1000$**

**note: pO is similar to pH in solution chemistry which measures affinity for protons,**

**$pH = -\log[H^+]$**

# Oxygen affinity of metals

| oxide | pO |
|---|---|
| $Au_2O_3$ | -5.5 |
| $Ag_2O_3$ | -3.3 |
| PtO | -1.3 |
| air | 0.7 |
| $IrO_2$ | 0.9 |
| $RhO_2$ | 4.2 |
| $Cu_2O$ | 9.6 |
| PbO | 12.7 |
| $H_2/H_2O=10^3$ | 13.6 |
| $CO/CO_2=10^3$ | 14.6 |
| CoO | 16.2 |
| NiO | 16.2 |
| $SnO_2$ | 19.7 |
| $H_2/H_2O=10^0$ | 20.1 |
| $MoO_2$ | 20.1 |
| FeO | 20.6 |
| $CO/CO_2=10^0$ | 20.6 |
| $WO_2$ | 21.2 |
| ZnO | 25.8 |

| oxide | pO |
|---|---|
| $H_2/H_2O=10^{-3}$ | 26.0 |
| $CO/CO_2=10^{-3}$ | 26.8 |
| $Na_2O$ | 28.9 |
| $Cr_2O_3$ | 30.1 |
| MnO | 32.6 |
| $Ta_2O_5$ | 33.2 |
| $SiO_2$ | 36.3 |
| TiO | 44.2 |
| $Al_2O_3$ | 47.2 |
| $ZrO_2$ | 47.2 |
| BaO | 48.6 |
| MgO | 52.0 |
| $Y_2O_3$ ($RE_2O_3$) | 52.0 |
| CaO | 55.5 |

## uses of pO tables:

- oxides with pO < 0 are unstable
  ex: $pO_2$ for $Au_2O_3$ = $3.16 \times 10^5$atm

- oxides with pO >> 0 are very stable
  ex: $pO_2$ for CaO = $3.16 \times 10^{-56}$ atm

- a metal will reduce any oxide with a pO smaller than its own.

ex: Mo (pO = 20.1) will reduce NiO(pO = 16.2)
(i.e. $MoO_2$ more stable than NiO)

ex: elements such as Pt, Ir, Rh will not reduce most metal oxides

## “buffer” gases

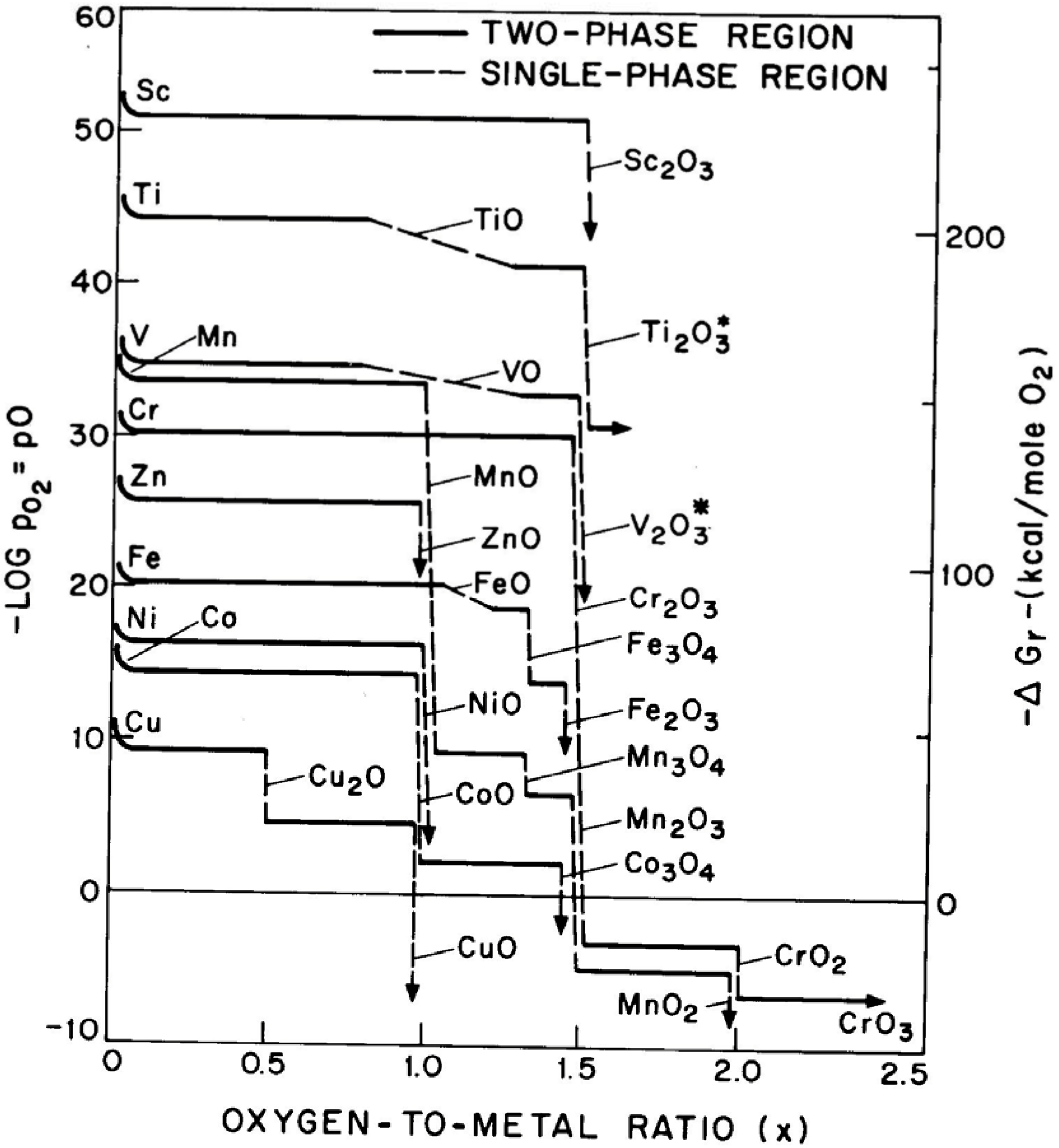
- $2H_{2(g)} + O_{2(g)} = 2H_2O_{(g)}$
- $2CO_{(g)} + O_{2(g)} = 2CO_{2(g)}$

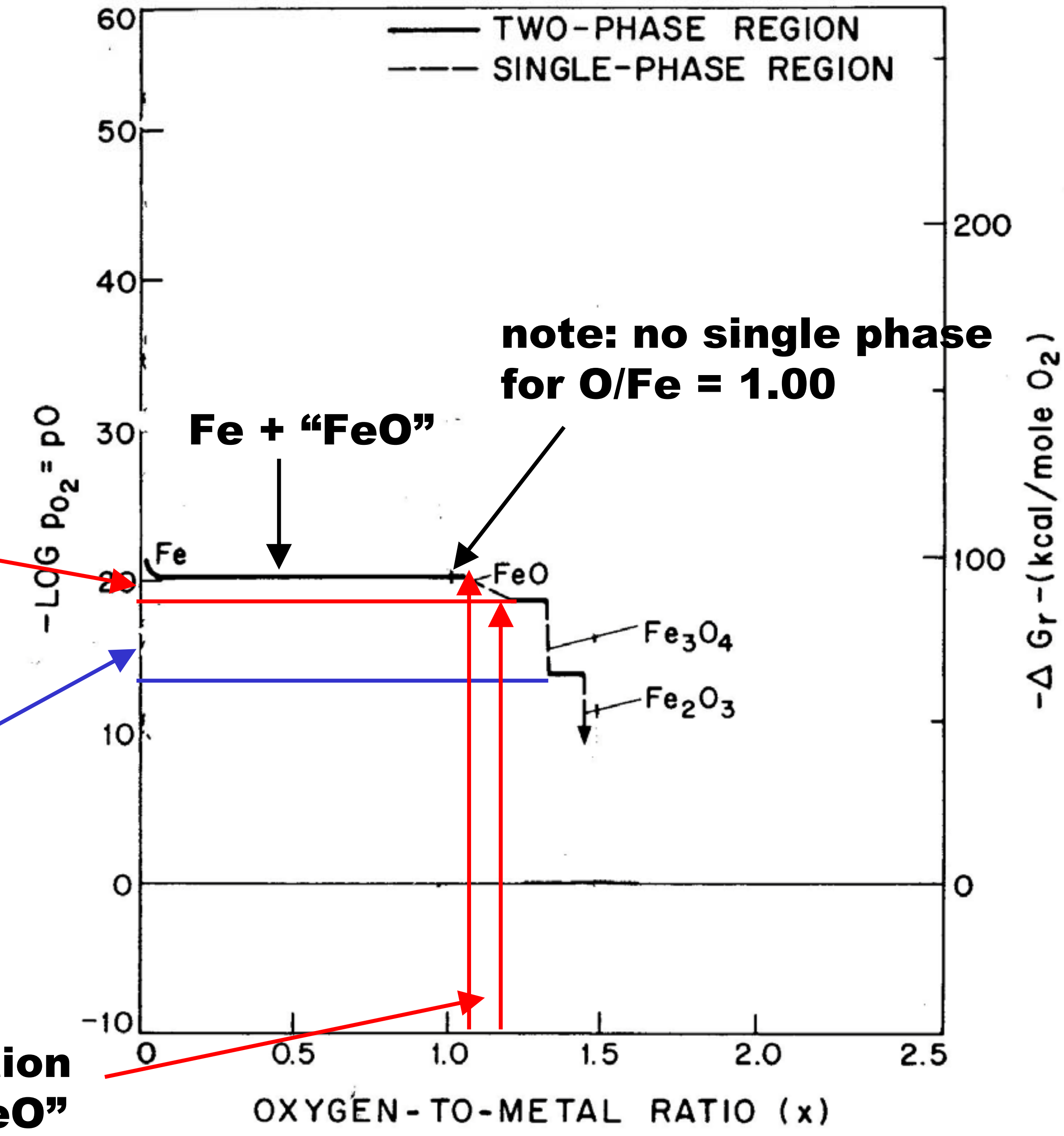
at a given T and $pH_2O/pH_2$ or $pCO_2/pCO$

$pO_2$ (or pO) will be fixed.

∴ $pO_2$(pO) can be controlled using

fixed gas ratios


TWO-PHASE REGION
SINGLE-PHASE REGION
$-\mathrm{LOG}\ p_{O_2} = pO$
60
50
40
30
20
10
0
-10
$-\Delta G_r$ -(kcal/mole $O_2$)
200
100
0
0
0.5
1.0
1.5
2.0
2.5
OXYGEN-TO-METAL RATIO (x)
Sc
$Sc_2O_3$
Ti
TiO
$Ti_2O_3^*$
V
Mn
VO
Cr
Zn
MnO
$V_2O_3^*$
ZnO
Fe
FeO
$Cr_2O_3$
Ni
Co
$Fe_3O_4$
NiO
$Fe_2O_3$
Cu
$Cu_2O$
$Mn_3O_4$
CoO
$Mn_2O_3$
$Co_3O_4$
CuO
$CrO_2$
$MnO_2$
$CrO_3$



**note: no single phase for O/Fe = 1.00**

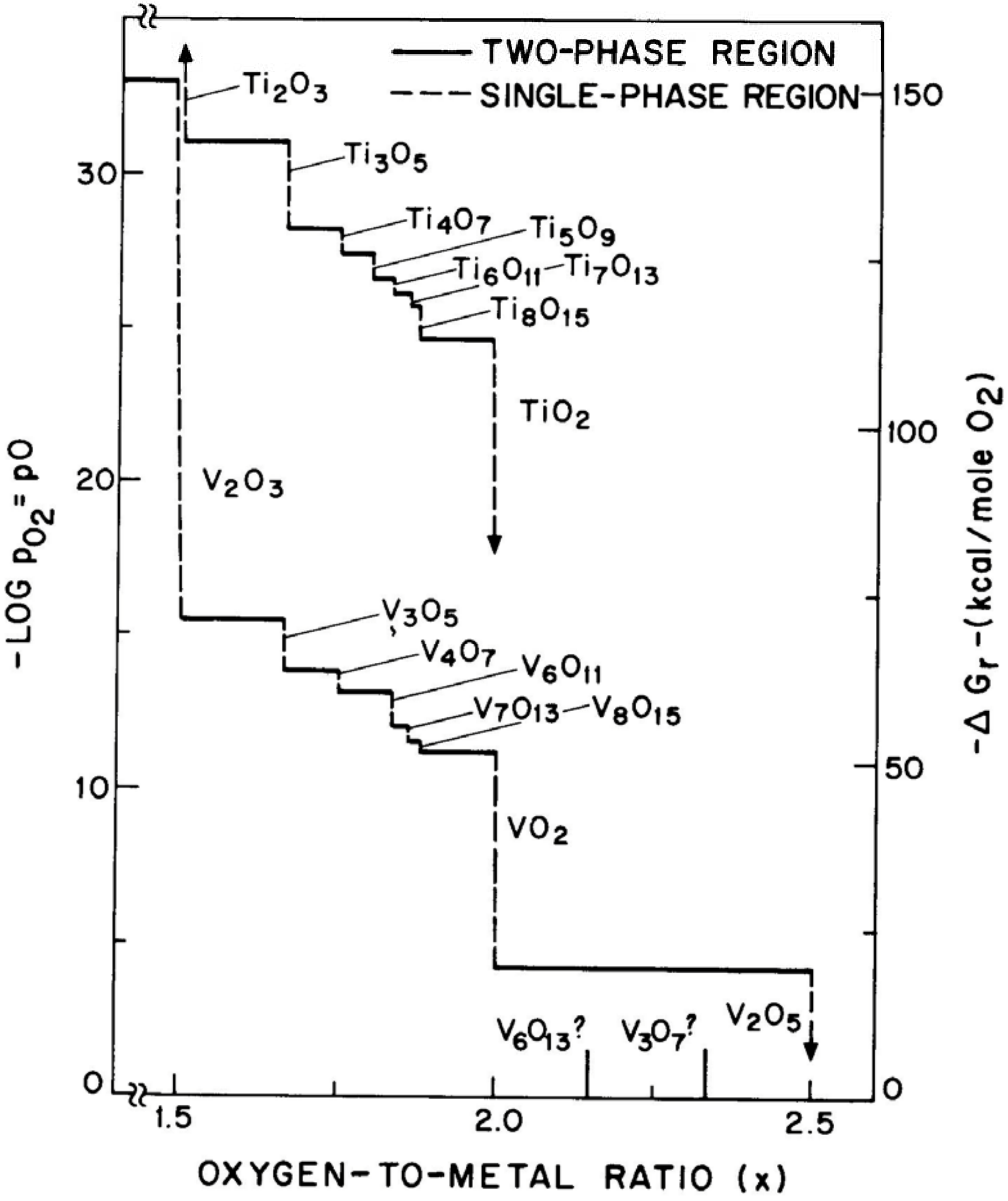
**Fe + "FeO"**

**existence range "FeO"**

**existence range $Fe_3O_4$**

**composition range "FeO"**

**$Fe_3O_4$ and $Fe_2O_3$ "line compounds"**



TWO-PHASE REGION
SINGLE-PHASE REGION
$Ti_2O_3$
$Ti_3O_5$
$Ti_4O_7$
$Ti_5O_9$
$Ti_6O_{11}$
$Ti_7O_{13}$
$Ti_8O_{15}$
$TiO_2$
$V_2O_3$
$V_3O_5$
$V_4O_7$
$V_6O_{11}$
$V_7O_{13}$
$V_8O_{15}$
$VO_2$
$V_6O_{13}$?
$V_3O_7$?
$V_2O_5$
$-LOG\ p_{O_2} = pO$
0
10
20
30
$-\Delta G_r$ -(kcal/mole $O_2$)
0
50
100
150
1.5
2.0
2.5
OXYGEN-TO-METAL RATIO (x)

## Examples:

**pyrochlores** $Ln_2^{3+}V_2^{4+}O_7$, $Ln_2^{3+}Mo^{4+}O_7$

$$2\ LnVO_4 \xrightarrow[CO/CO_2]{1400^oC} Ln_2V_2O_7$$

pO = 6.1 - 6.9

$Ln_2Mo_2O_7$

$$Ln_2O_3 + MoO_2 \xrightarrow[CO/CO_2 = 1]{1350^oC} Ln_2Mo_2O_7$$

Mat. Res. Bull. 14 (1979) 13
Solid State Communications, 59, (1986) 895-897

# B. Crystal growth methods.

1. Bridgeman
2. Czochralski
3. Floating zone
4. Flux
5. Hydrothermal

## Crucible methods

1. Bridgeman
2. Czochralski
4. Flux
5. Hydrothermal

## Crucible-free methods

3. Floating zone

# Crucible methods - materials

- crucible - melt compatibility

| Metal | m.p.(C°) |
|---|---|
| Pt | 1772 |
| Rh | 1966 |
| Ir | 2410 |
| Mo | 2617 |
| W | 3410 |
| Re | 3180 |
| Nb | 2468 |
| Ta | 2996 |

| Metal oxide | m.p.(C°) |
|---|---|
| $Al_2O_3$ | 2072 |
| $TiO_2$ | 1855 |
| MgO | 2852 |
| $Fe_3O_4$ | 1594 |
| $V_2O_3$ | 1967 |
| $Cr_2O_3$ | 2330 |
| $SiO_2$ | 1423 |

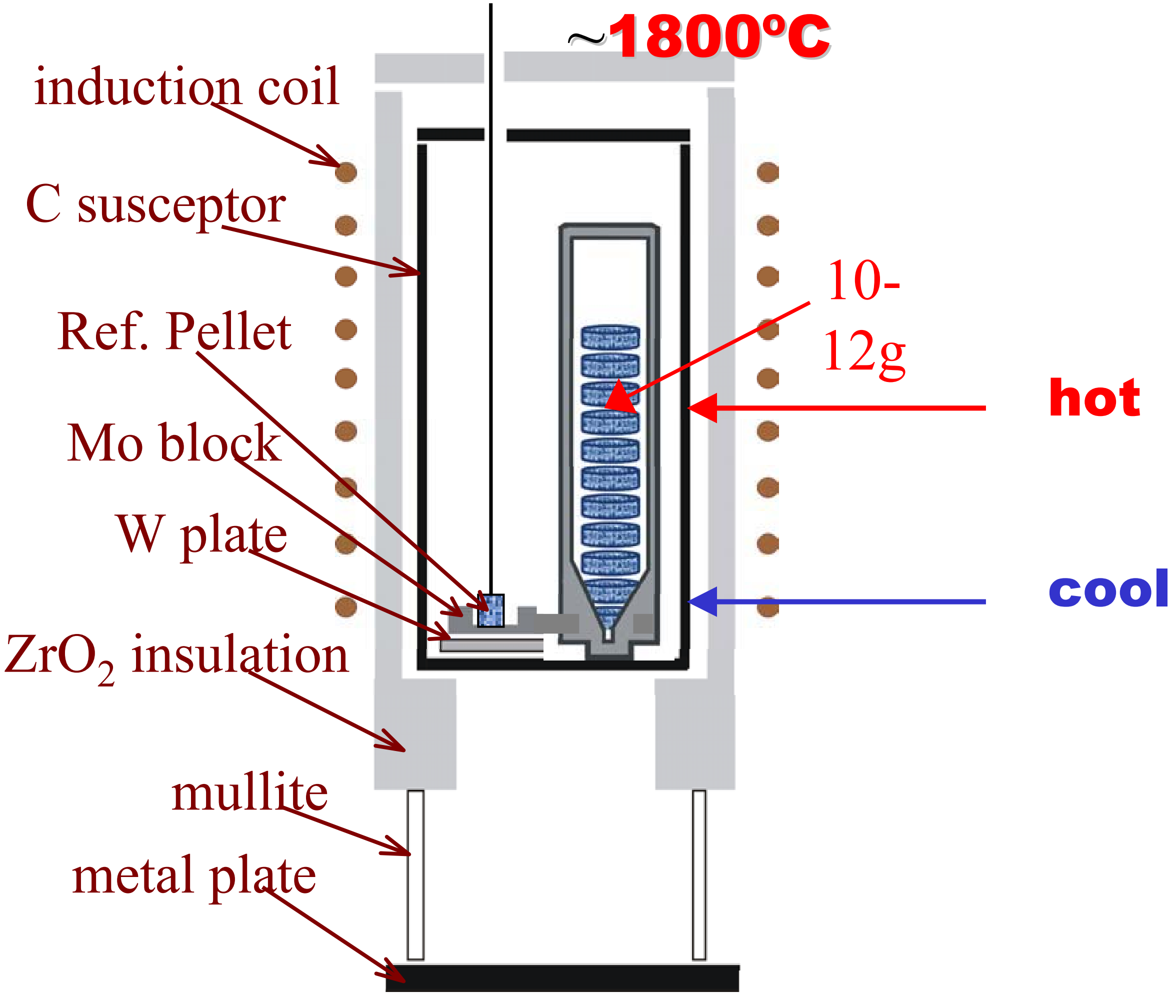
# Ex: Bridgeman growth of $Nd_{1-x}TiO_3$ in a Mo crucible

[PRB 74 (2006) 104419]

**cooling rate:**

**1 - 5°C/hr**

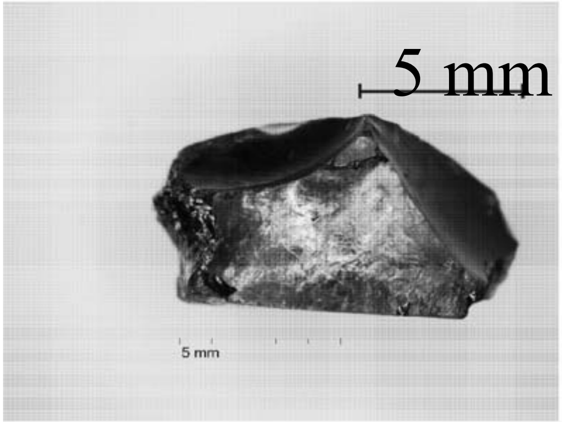
## *Bridgeman method*



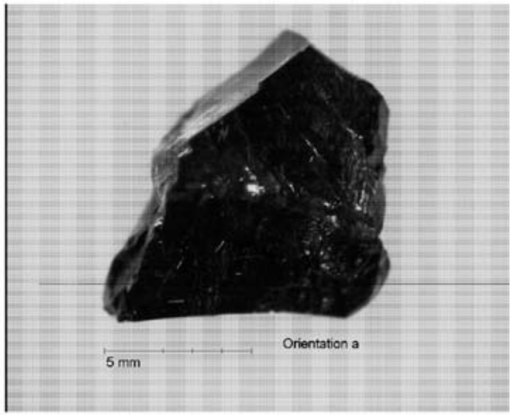
***x*** **≈ 0.10, 0.04**

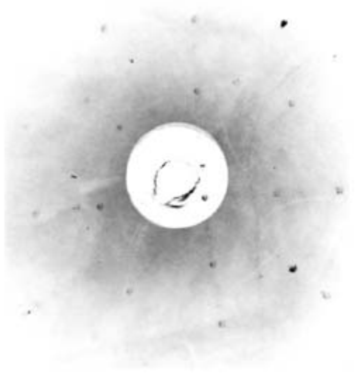
# Bridgeman crystals - $Nd_{1-x}TiO_3$

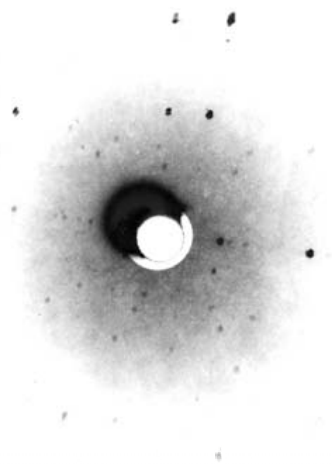
**x = 0.10**



**X = 0.04**



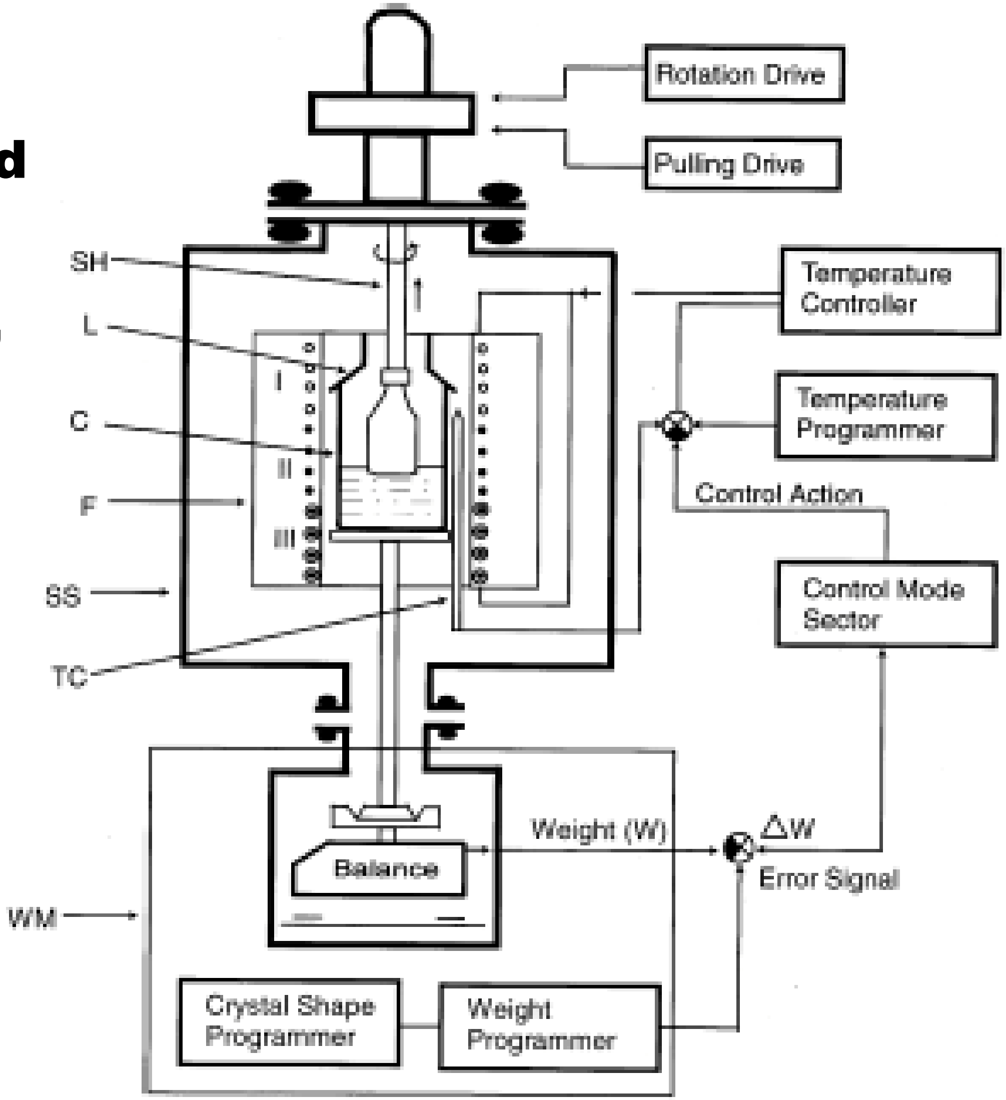




**5 mm = 5 x $10^6$ nm**

# Typical modern Czochralski (a.k.a. crystal pulling) configuration

- **melt contained in crucible.**
- **"seed crystal" lowered to contact melt.**
- **seed crystal slowly raised, crystal grows on seed and "pulled" from melt.**



J. Cryst. Growth 197 (1999) 865

# $Bi_4Ge_3O_{12}$

Grown from a Pt crucible @ 1300°C

# Flux growth,
# i.e. precipitation from “high temperature”solution.

- **In general oxides are insoluble in most simple solvents ($H_2O$ for example) but often can be “ dissolved” in complex mixtures called fluxes.**

- **flux compositions designed to be molten below ~ 1000°C and above ~ 600 °C.**

- **solubility not easy to predict but many recipes exist.**

- **Procedure:**
  1. **dissolve oxide in flux by heating to ~ 1000°C**
  2. **“soak” for period of ~ hrs.**
  3. **Cool slowly,(~ °C/hr)**
  4. **crystals precipitate - often many nucleation sites**

# Flux growth of some antimonates, $ASb_2O_6$, A = Mn, Co, Ni,Cu [J.Cryst. Growth 154 334-338 (1995)]

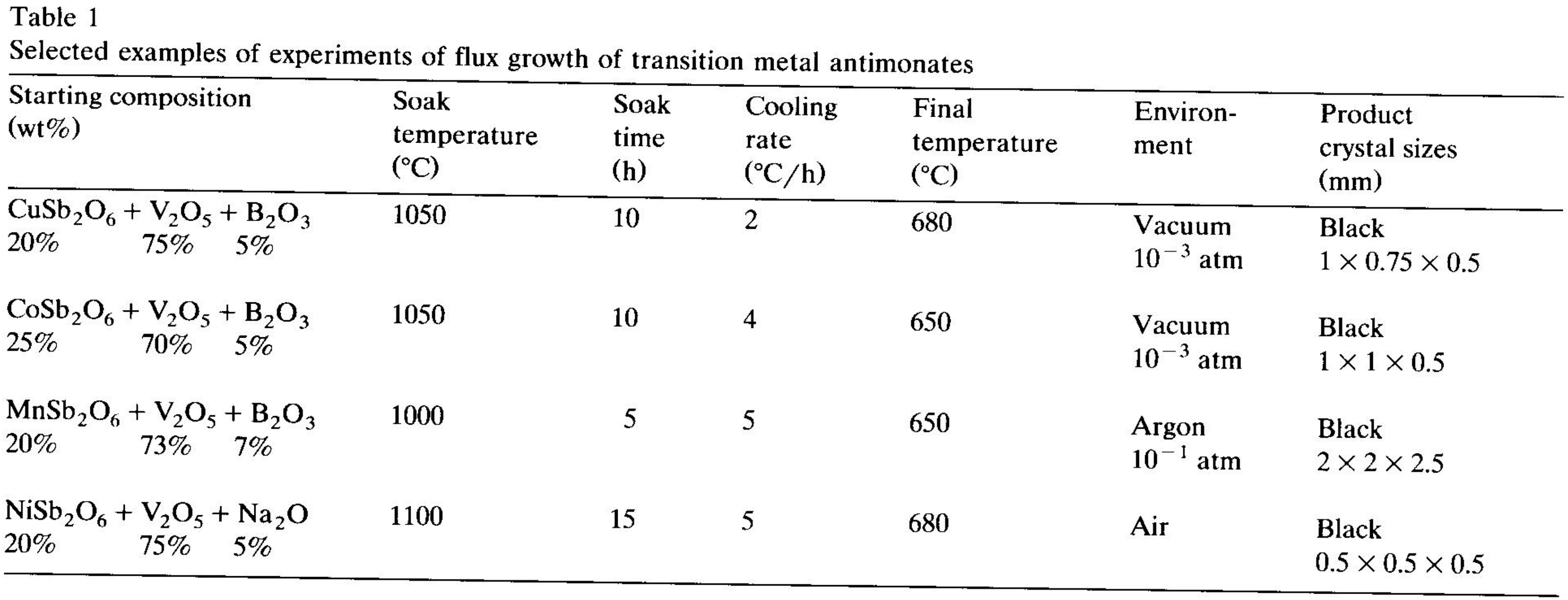


Table 1
Selected examples of experiments of flux growth of transition metal antimonates

| Starting composition (wt%) | Soak temperature (°C) | Soak time (h) | Cooling rate (°C/h) | Final temperature (°C) | Environ-ment | Product crystal sizes (mm) |
|---|---|---|---|---|---|---|
| $CuSb_2O_6 + V_2O_5 + B_2O_3$<br>20% 75% 5% | 1050 | 10 | 2 | 680 | Vacuum<br>$10^{-3}$ atm | Black<br>1 × 0.75 × 0.5 |
| $CoSb_2O_6 + V_2O_5 + B_2O_3$<br>25% 70% 5% | 1050 | 10 | 4 | 650 | Vacuum<br>$10^{-3}$ atm | Black<br>1 × 1 × 0.5 |
| $MnSb_2O_6 + V_2O_5 + B_2O_3$<br>20% 73% 7% | 1000 | 5 | 5 | 650 | Argon<br>$10^{-1}$ atm | Black<br>2 × 2 × 2.5 |
| $NiSb_2O_6 + V_2O_5 + Na_2O$<br>20% 75% 5% | 1100 | 15 | 5 | 680 | Air | Black<br>0.5 × 0.5 × 0.5 |

**$V_2O_5 + B_2O_3$ flux - m.p. ($V_2O_5$) ~ 700°C.**

**quartz ($SiO_2$) crucibles**

*f Crystal Growth 154 (1995) 334–338*

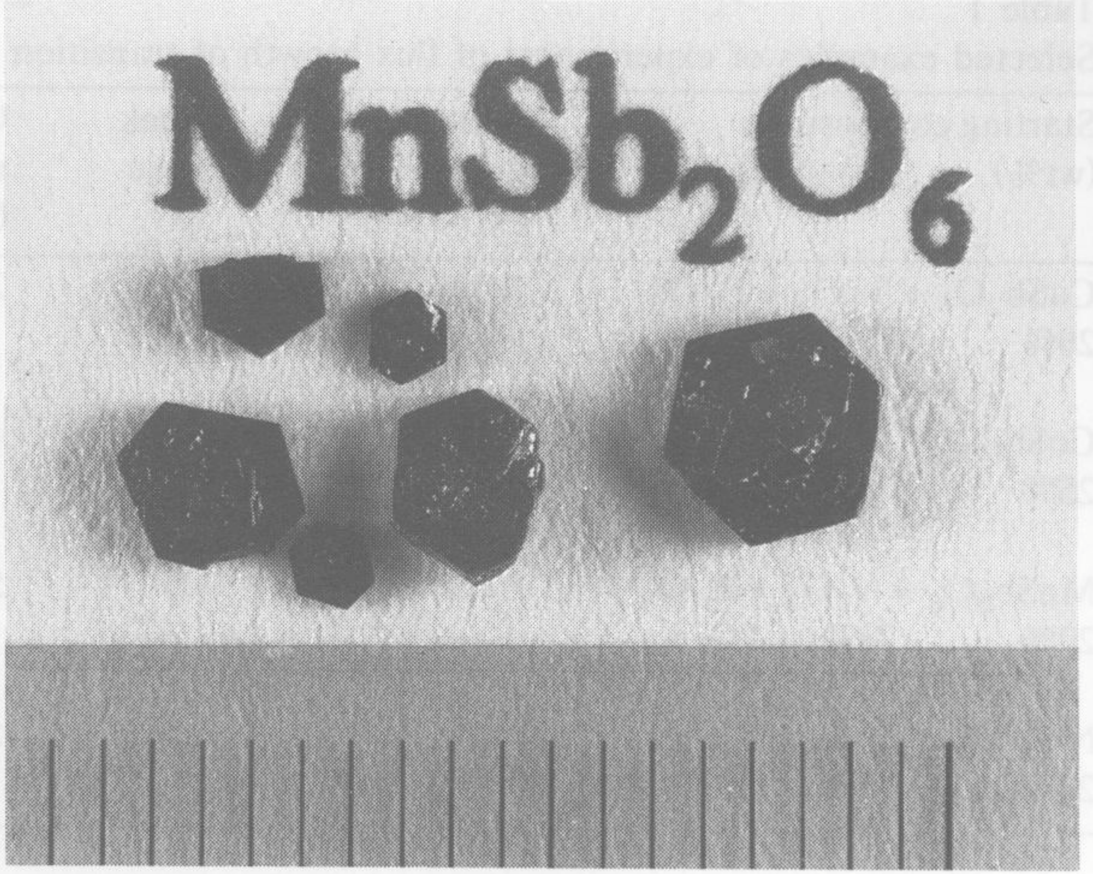
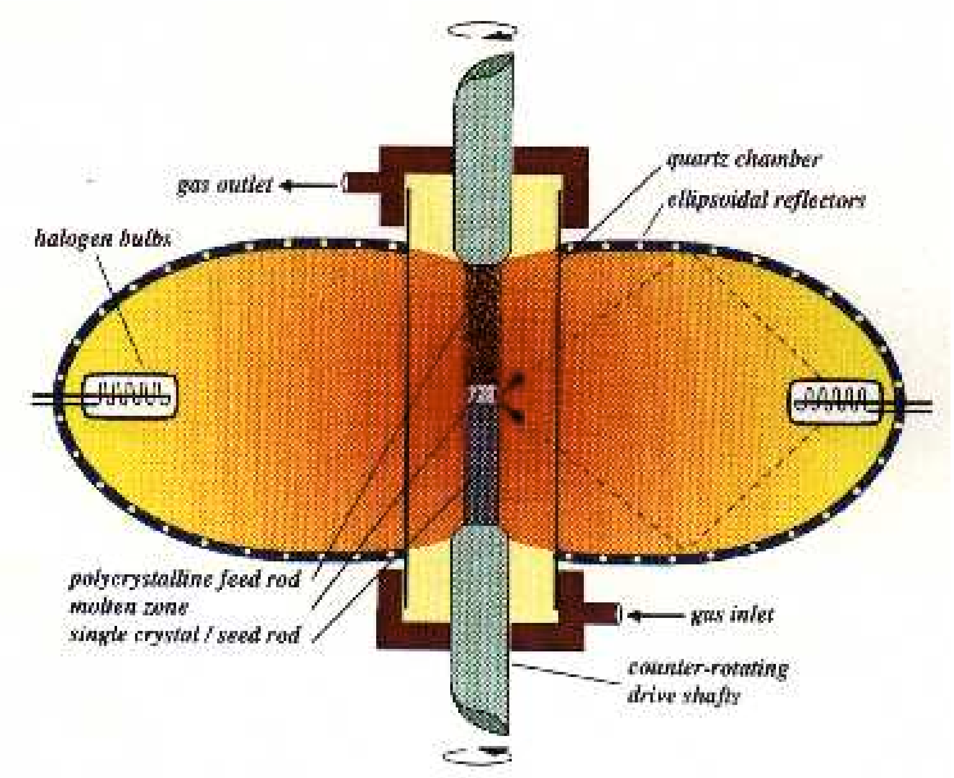


Fig. 2. Single crystals of $MnSb_2O_6$ grown from $V_2O_5$–$B_2O_3$ flux under 0.1 atm of argon. Divisions are 0.5 mm.

## Problems with crucible-based methods

- melt - crucible reactivity
- cost of Pt, Ir, Rh crucibles
- flux inclusions
- Czochralski and Bridgeman difficult as oxide m.p. increases

# A recent panacea!  The lamp image floating zone method.



**NEC SC-N35HD**

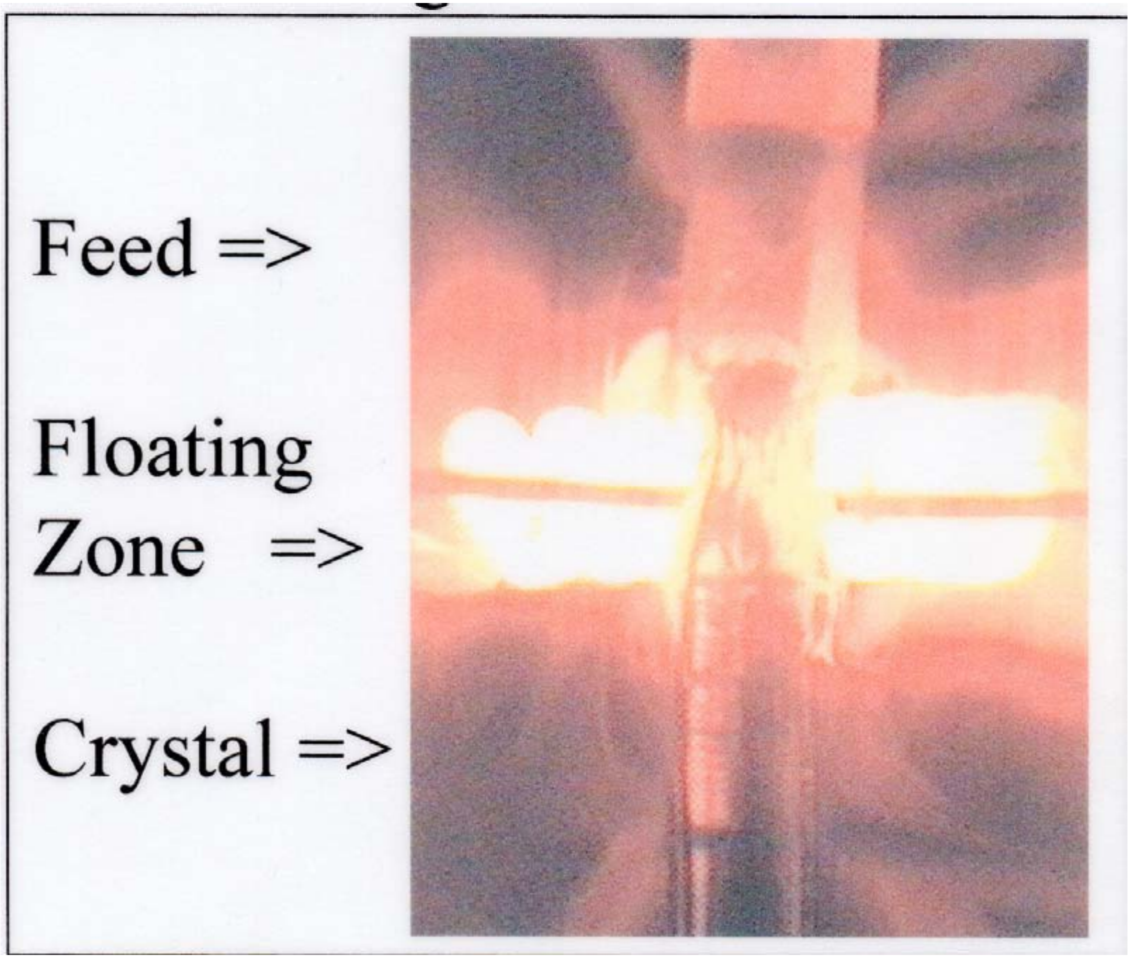
**Energy from IR sources focused using mirrors to a small volume, ~ mm, on a solid, dense rod, creating a molten zone. Molten zone moved through length of rod often resulting in growth of a crystal without a crucible!**

- **2 lamp and 4 lamp versions (CSI-FZ)**

- **Xenon lamps replace halogen lamps for higher temperatures ~ 2800°C**

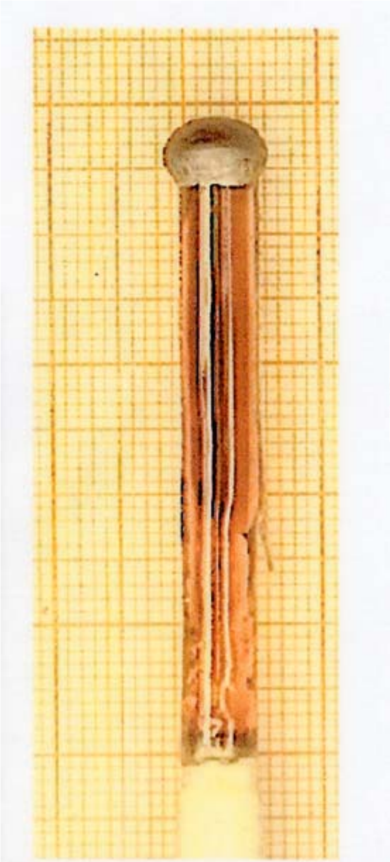
- **operate under turbo-pump vacuum, $10^{-9}$ atm**

- **or pressures up to ~ 10 atm of variety of gases**



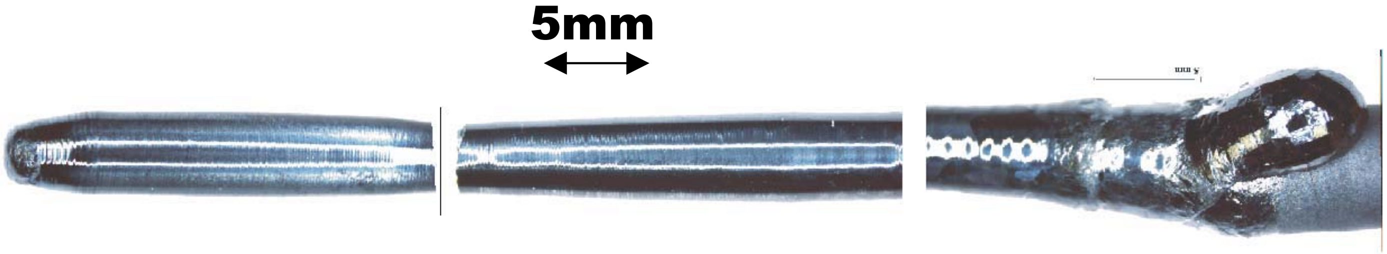

10-12cm
feed ~ 13g

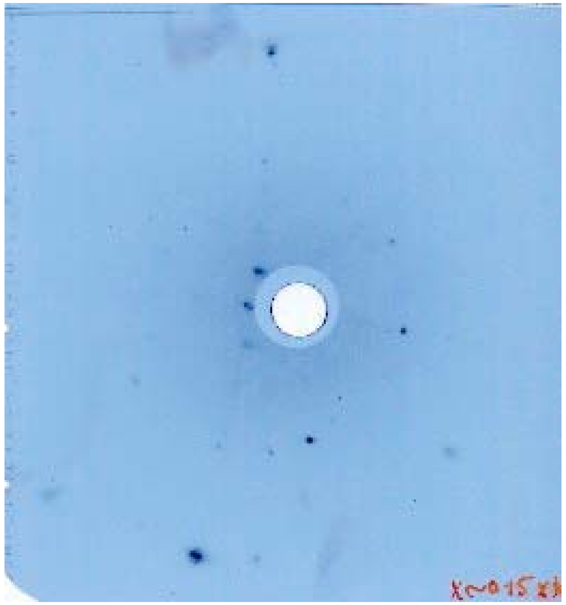
5-8 cm seed
~10g



Result:
$(Y/Tb)_2Ti_2O_7$

## $Nd_{0.85}TiO_3$





## Hydrothermal techniques

- while oxides are not usually soluble in $H_2O$ under ambient conditions, this can change under modest pressure of a few $10^3$ atms.

- $H_2O$, the oxide and some “mineralizers” are sealed into a Au, Ag or Pt crucible and heated to ~ 200°C - 300°C in an autoclave.

- Crystals (often small) result.

- but giant quartz crystals ($SiO_2$) are grown hydrothermally (simulating geothermal conditions in nature)

# $AFe_3(SO_4)_2(OH)_6$ - jarosite

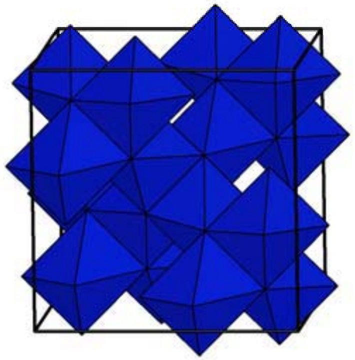
[PRB 67 (2003) 064401]
[NatureMater. 4 (2004) 323]

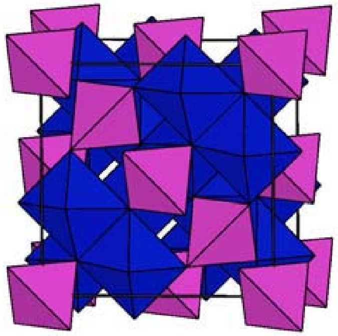
**single crystals have been grown hydrothermally up to 10 mm, large enough for inelastic neutron scattering.**

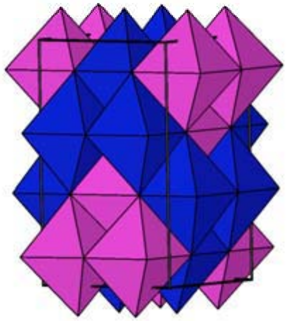
# “Soft” chemical routes to metastable phases

## ex: $Li_xMn_2O_4$, $x = 0 \longrightarrow 2$.

$$\lambda\text{ - }MnO_2 \xleftarrow{\text{- Li}} \underset{\text{spinel}}{LiMn_2O_4} \xrightarrow{\text{+ Li}} Li_2Mn_2O_4$$







**Li can be added or removed from $LiMn_2O_4$ @ room T using either electrochemical or chemical means leaving the frustrated Mn pyrochlore lattice intact.**

**λ - $MnO_2$ and $Li_2Mn_2O_4$ cannot be prepared by other means.**