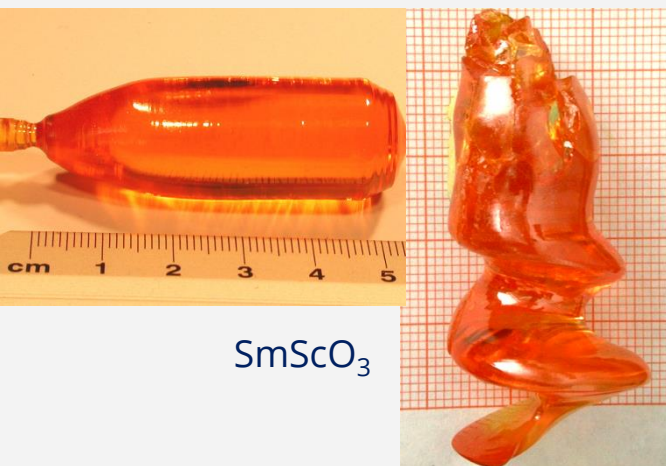


Thermal Analysis and Thermodynamic Calculations in Rare-Earth Oxide Based Systems

D. Klimm, Leibniz-Institut für Kristallzüchtung (IKZ) Berlin

Outline:

1. Introduction
2. $\text{Y}_3\text{Al}_5\text{O}_{12}$ ("YAG" = yttrium aluminum garnet)
3. REScO_3 and related rare-earth scandates (distorted perovskites)
4. Summary



SmScO_3

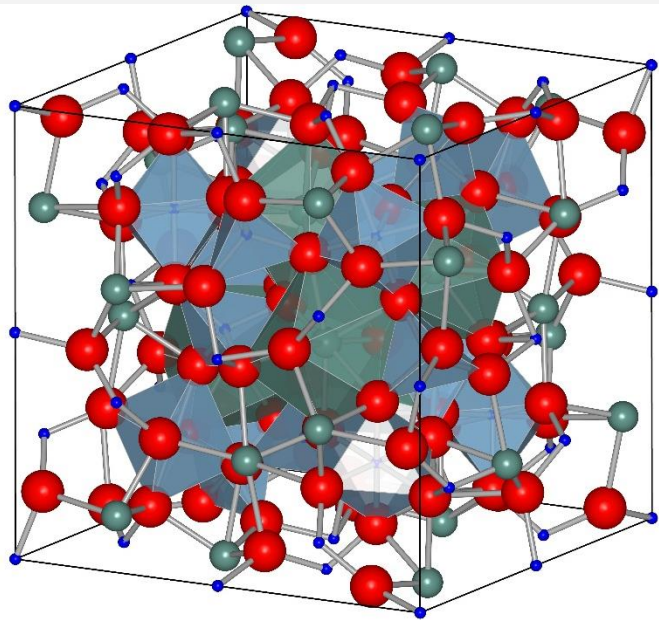


$\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$

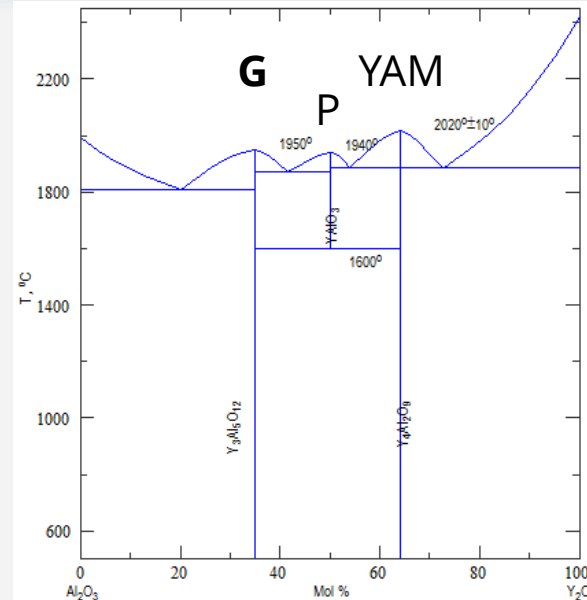


Intermediate compounds in $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3$ systems:

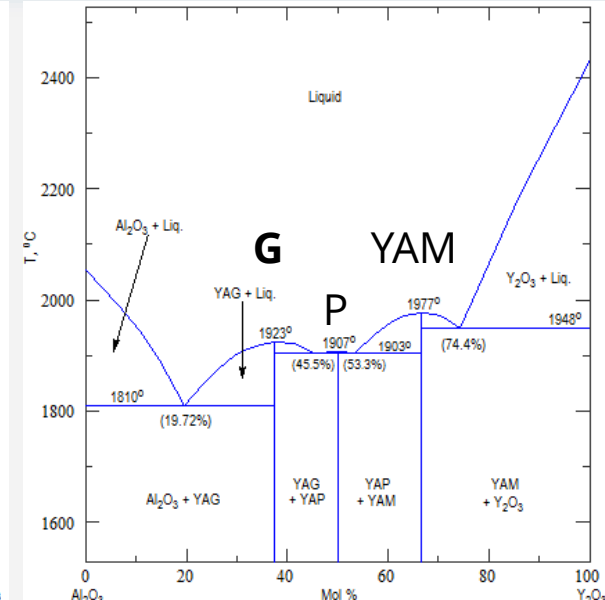
- **Garnet** ($\text{Y}_3\text{Al}_5\text{O}_{12}$, **G**)
- Perovskite (YAlO_3 , **P**)
- Monoclinic ($\text{Y}_4\text{Al}_2\text{O}_9$, "YAM")



One unit cell of $\text{Y}_3^{[8]}\text{Al}_5^{[6]}\text{Al}_2^{[4]}\text{O}_{12}$, space group $Ia\bar{3}d$



Bondar et al., *Neorg. Mater.* **20** (1984) 257-26 (experimental).



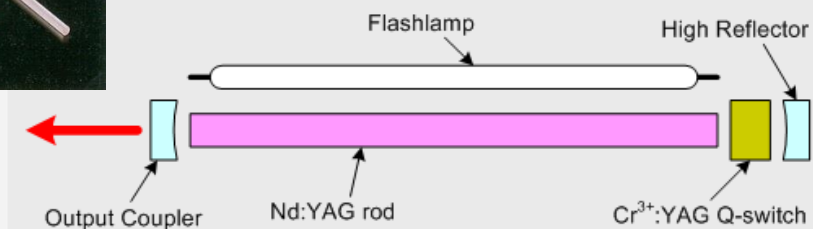
Fabrichnaya et al., *Scand. J. Metall.*, **30** (2001) 175-183 (assessed).

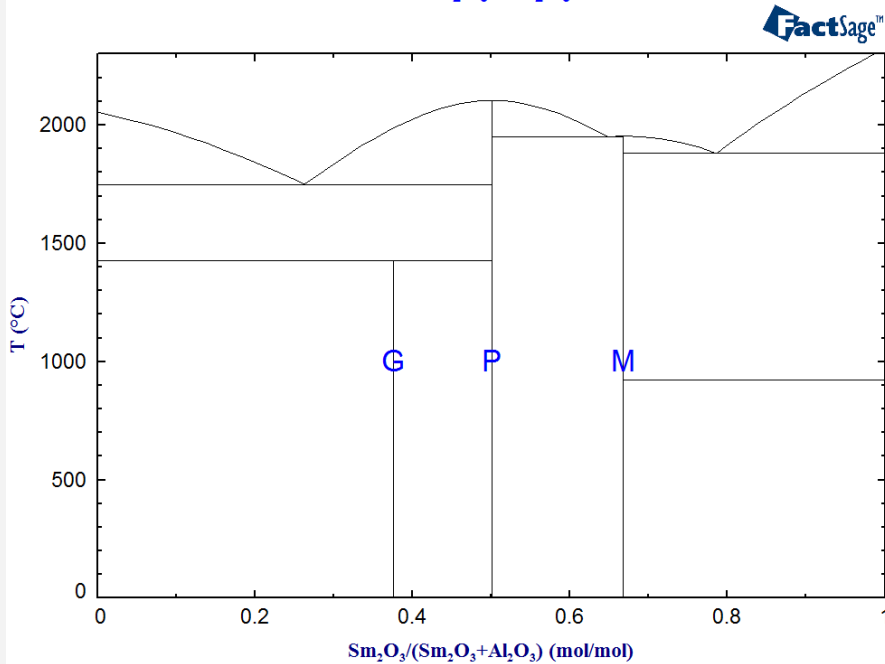
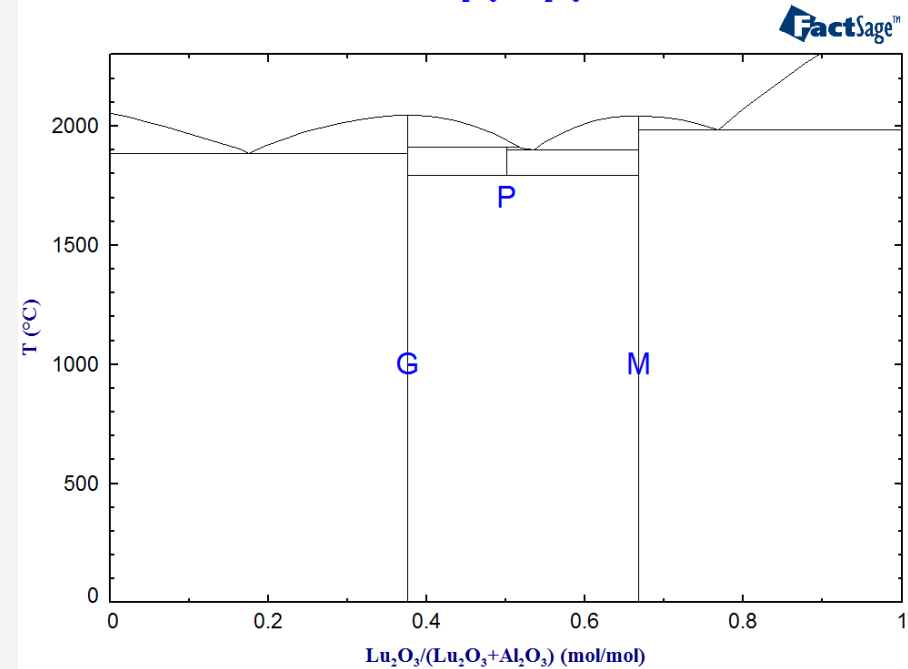


Q: How much Y^{3+} can be exchanged by Nd^{3+} ? (Doped YAG crystals up to 2.5 at-% Nd available. $\text{Nd}_3\text{Al}_5\text{O}_{12}$ as pure phase yet unknown.)

Q-Switched Nd:YAG Laser

<http://c4r0.elektroda.eu>



$\text{Sm}_2\text{O}_3 - \text{Al}_2\text{O}_3$  $\text{Lu}_2\text{O}_3 - \text{Al}_2\text{O}_3$ 

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm ☼	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.91	140.12	140.91	144.24	144.91	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.05	174.97
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium

(Y)

Garnets more stable

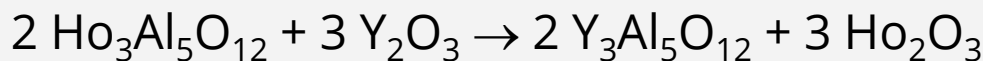
Perovskites more stable

- Problem: Thermodynamic data for all systems $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3$ (solids & melts) are available in FactSage (Wu, Pelton, *J. Alloy. Comp.* 179 (1992) 259–287.), except for $\text{RE} = \text{Y}$.
- Ternary interactions $\text{RE}_2\text{O}_3\text{-RE}'_2\text{O}_3\text{-Al}_2\text{O}_3$ almost not available.

Getting data for $\text{Y}_3\text{Al}_5\text{O}_{12}$:

Ionic radii: Y^{3+} in 8-fold coordination: 115.9 pm
 Ho^{3+} in 8-fold coordination: 115.5 pm

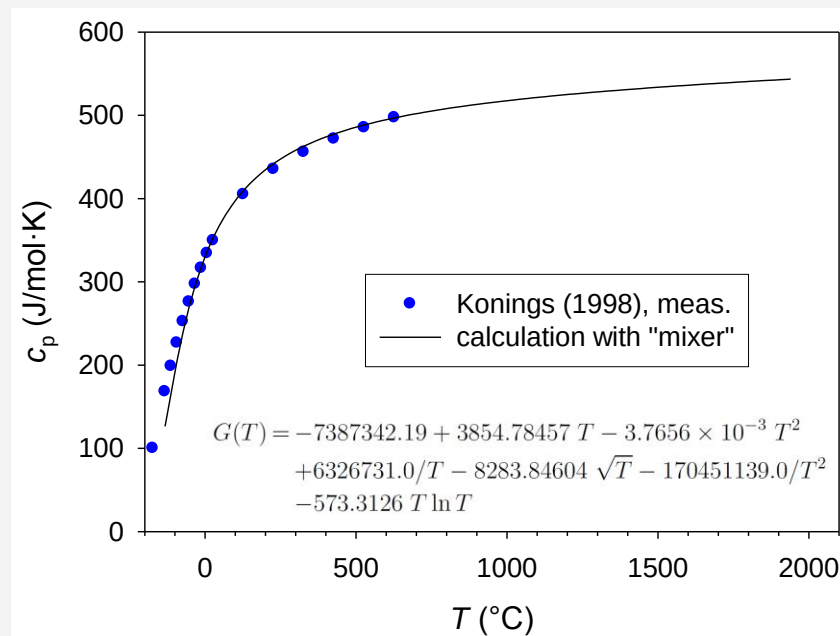
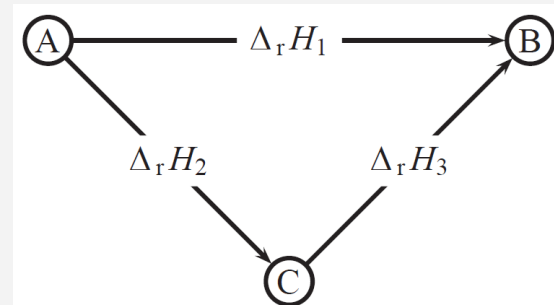
“Mixer” in the FactSage compound module:
 (actually, derived from Hess’s law)



data for $\text{Y}_3\text{Al}_5\text{O}_{12}$ measured by

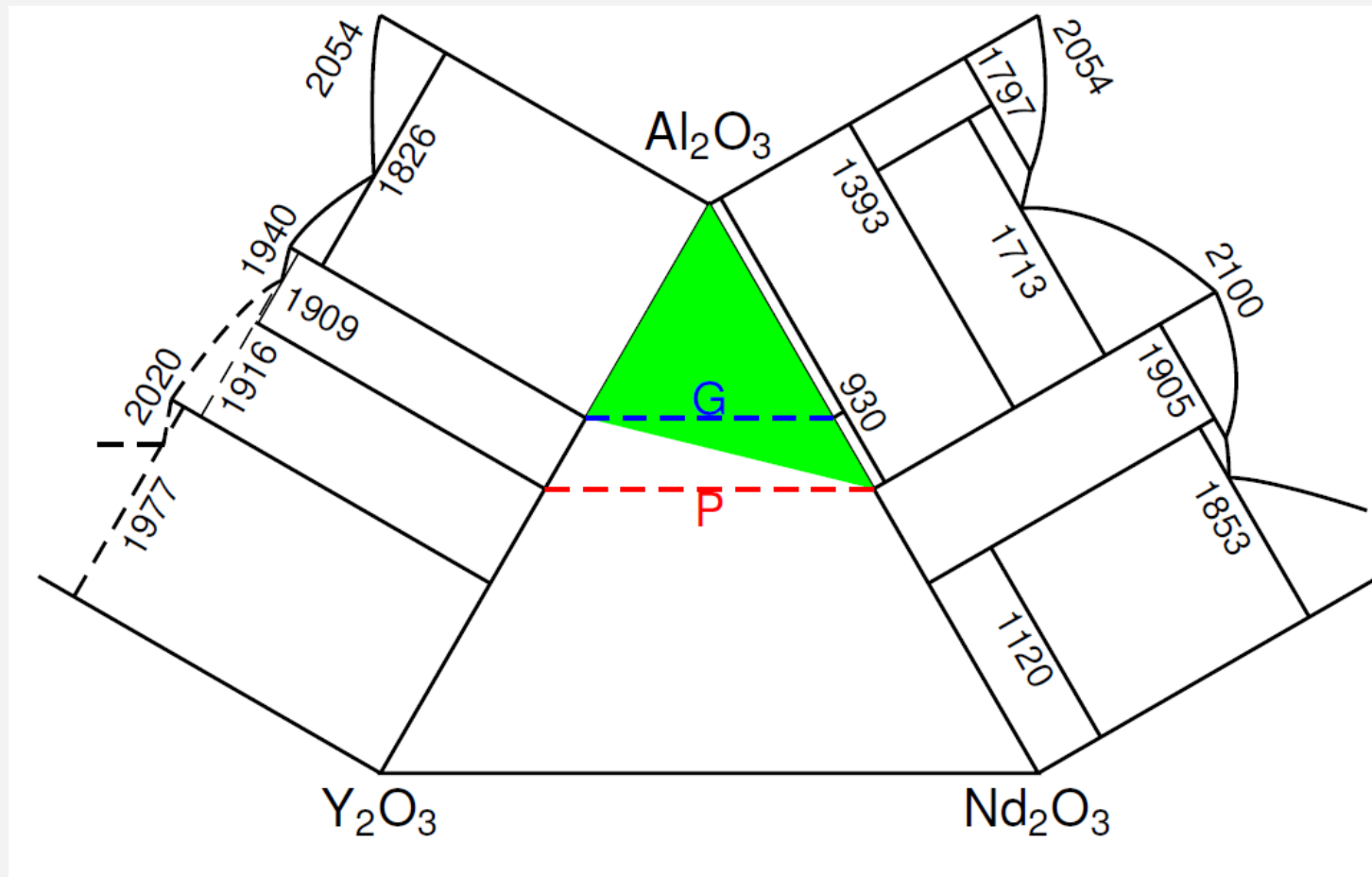
Konings et al., *thermochimica acta* 313 (1998) 201-206:

- adiabatic calorimetry from 5 to 420 K
- drop calorimetry from 470 to 880 K
- (*J. Alloys. Compd.* 436 (2007) 204-208)



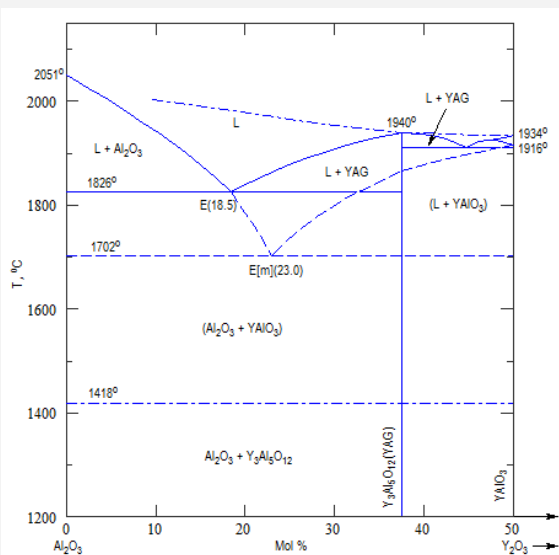
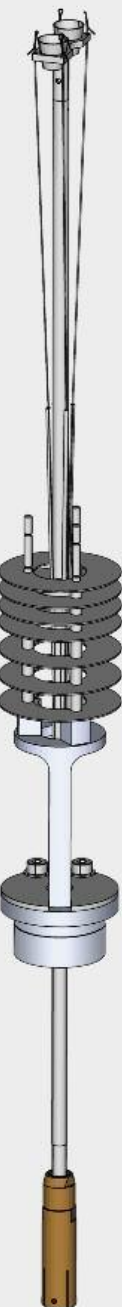
The concentration triangle $\text{Al}_2\text{O}_3 - \text{NdAlO}_3 - \text{Y}_3\text{Al}_5\text{O}_{12}$:

- Congruent melting is a condition for being component of a subsystem.
- "G" section: $(\text{Y}_{1-x}\text{Nd}_x)_3\text{Al}_5\text{O}_{12}$ garnets. No thermodynamic data $\rightarrow$ ideal solution as approximation
- "P" section: $(\text{Y}_{1-x}\text{Nd}_x)\text{AlO}_3$ perovskites. Again ideal solution as simple model.
- $r_{\text{Y}^{3+}}^{[8]} = 115.9 \text{ pm}$, $r_{\text{Nd}^{3+}}^{[8]} = 124.9 \text{ pm}$

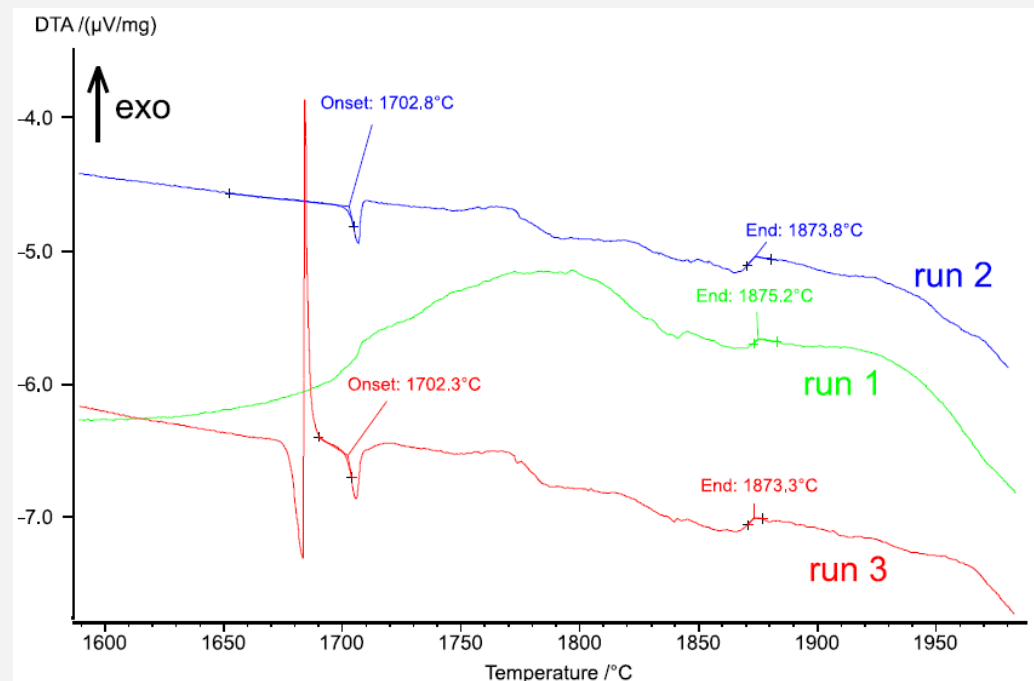


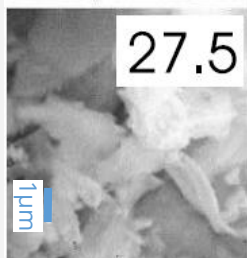
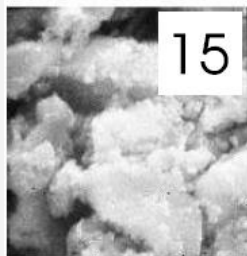
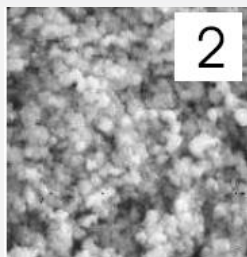
DTA experiments on the "G" section

- NETZSCH STA 409C with graphite furnace. 12-18 mg substance in W crucible. 3 heating/cooling cycles. Sample $(Y_{0.75}Nd_{0.25})_3Al_5O_{12}$ is shown.
- For $T \approx 1870^\circ\text{C}$ an offset is observed in all runs. T_{end} drops with x and marks the liquidus.
- For all samples $x \geq 0.25$ (except 1st heating) a sharp endothermal peak near 1700°C , attributed to melting. T drops slightly for larger x.
- DTA curves exhibit sometimes non-reproducible exothermal peaks on heating $\rightarrow$ non-equilibrium (cf. Caslavsky).



Caslavsky, *J. Mater. Sci.*,
15 (1980) 1709-1718.



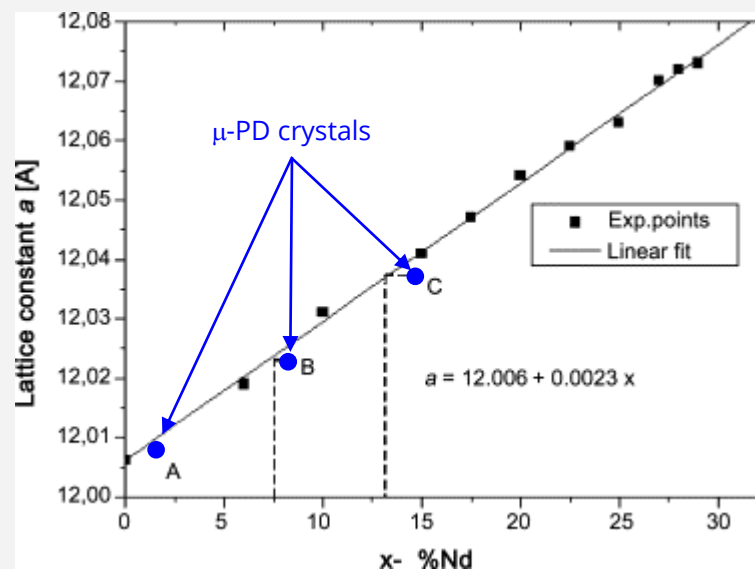
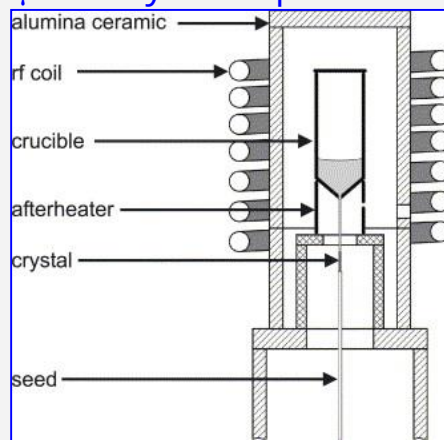


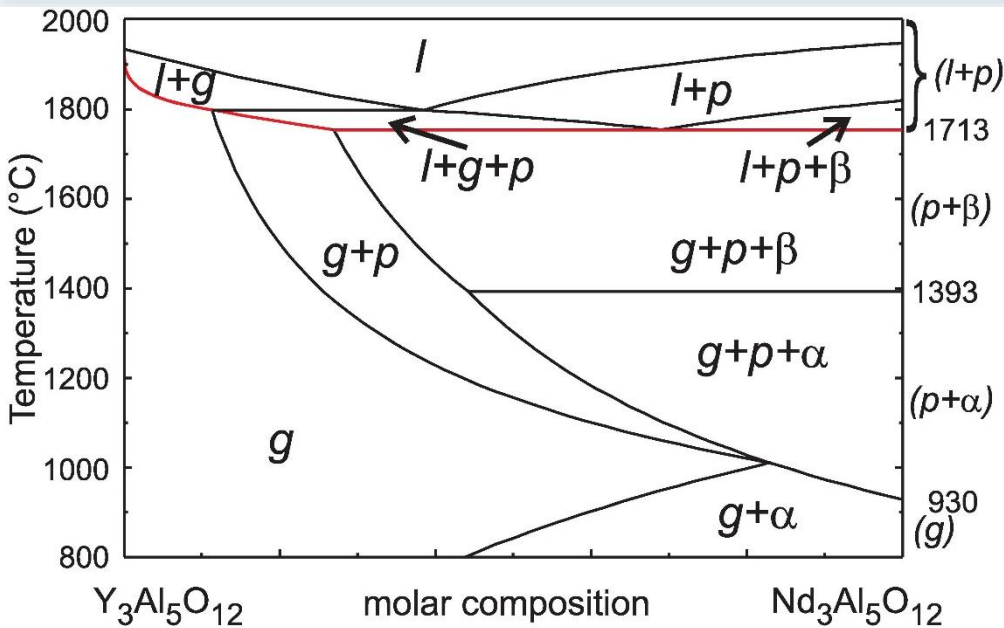
X-ray experiments on the "G" section $(Y_{1-x}Nd_x)_3Al_5O_{12}$ with nanopowders

- $Al(NO_3)_3$ dissolved in water
- $Y_2O_3 + 6 CH_3COOH \rightarrow 2 Y(CH_3COO)_3 + 3 H_2O$ (Nd_2O_3 analogously)
- 1,2-ethanediol ("ethylene glycole") added as complexing agent, drying by slow evaporation
- ground + preheated at $800^\circ C$, then annealed $\leq 1200^\circ C$
- "Garnet compositions" with 0-100 at-% Nd were prepared. (Numbers in the micrographs give Nd concentration in %.)
- "Garnet compositions" up to 27.5 at-% Nd were single phase; above also $(Nd,Y)AlO_3$ perovskite was found.
- Garnet: $a_0 = 12.006 + 0.0023 x$
(a_0 : lattice constant in Å;
 x : molar fraction of Nd).

➤ Why only $x \leq 0.025$ during Czochralski growth?

➤ μ -PD crystals up to 14%!





l – liquid

g – garnet

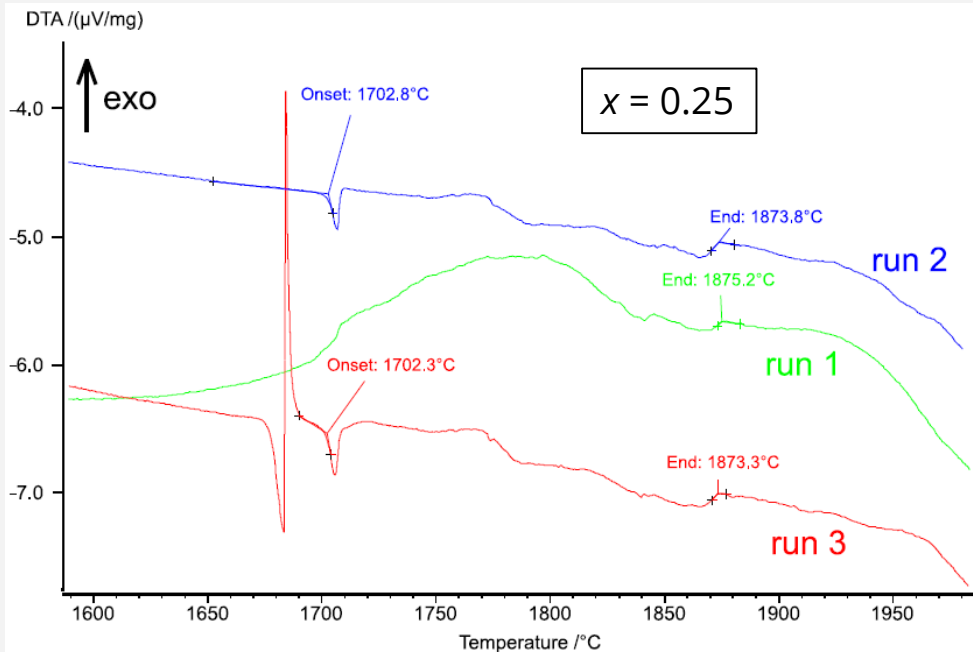
p – perovskite

α – α -Al₂O₃ (corundum)

β – “ β alumina” = Al₁₁NdO₁₈

The red line marks onset of melting.

← garnet section calculated under the assumption of ideal miscibility in the “*g*”, “*p*”, and “*l*” phase.



Summary Nd:Y₃Al₅O₁₂ garnet

- The solubility of Nd³⁺ in YAG is very high: 27.5% at $\approx 1200^\circ\text{C}$ proven, the ideal model proposes even $\approx 80\%$ around 1000°C .
- The much smaller doping limit $\approx 2.5\%$ during melt growth results from segregation during crystallization.
- Metastability in the subsolidus likely, e.g., resulting from garnet-perovskite transitions.

"Strain engineering" with distorted perovskites

(submitted to Cryst. Res. Technol.)

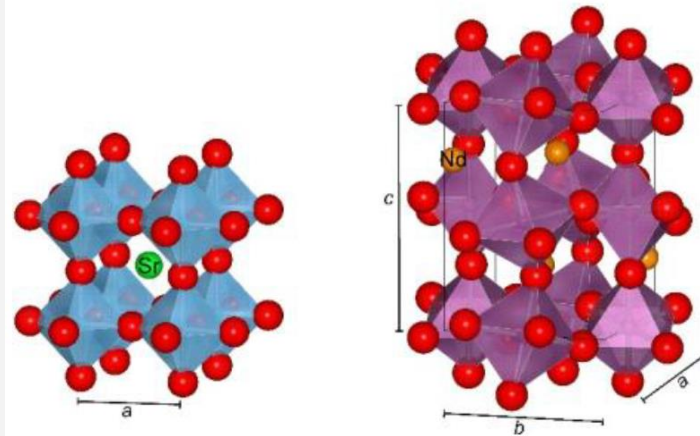
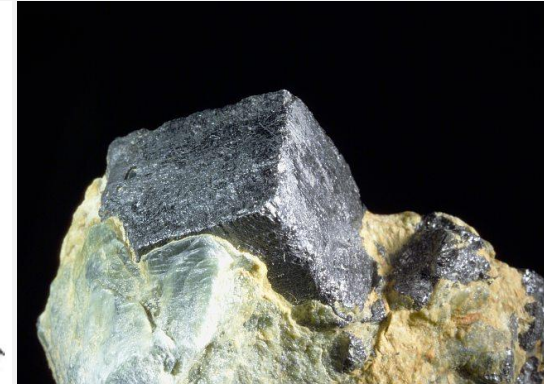


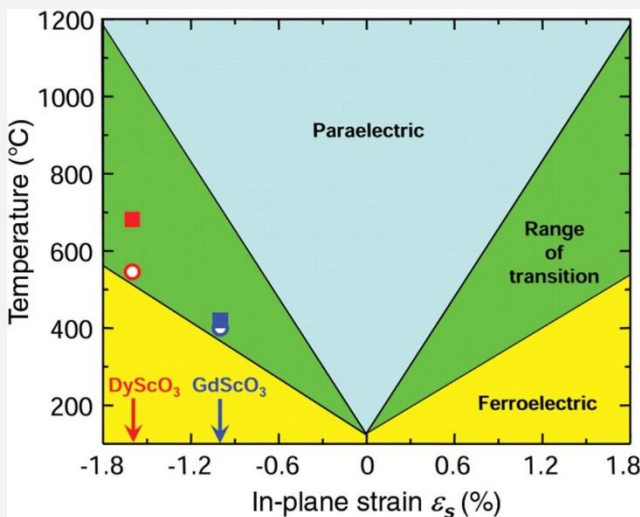
Figure 1 Left: One (cubic) unit cell of SrTiO_3 [12] contains 1 formula unit. Right: One (orthorhombic) unit cell of NdScO_3 [13] contains 4 formula units.



Perovskite CaTiO_3
Ахматовская копъ (Ural)

K.J. Choi et al., *Science* 306 (2004) 1005:

"Biaxial compressive strain has been used to markedly enhance the ferroelectric properties of BaTiO_3 thin films. This strain, imposed by coherent epitaxy, can result in a ferroelectric transition temperature nearly 500°C higher and a remanent polarization at least 250% higher than bulk BaTiO_3 single crystals. "

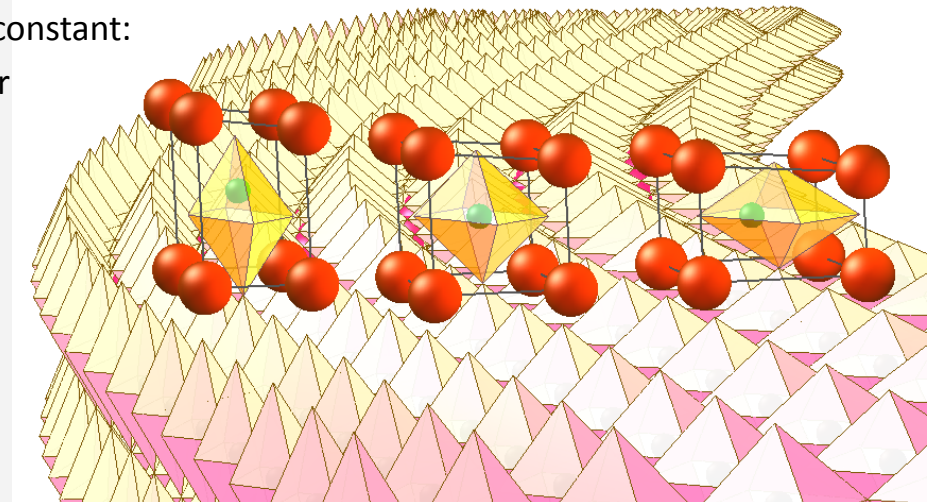


Pseudocubic lattice constant:

$$a_{pc} = \frac{1}{2}\sqrt{a^2 + b^2} \quad \text{or}$$

$$a_{pc} = \frac{1}{2}c \quad \text{or}$$

$$a_{pc} = \sqrt[3]{\frac{1}{4}abc}$$



courtesy D. Schlom, Cornell

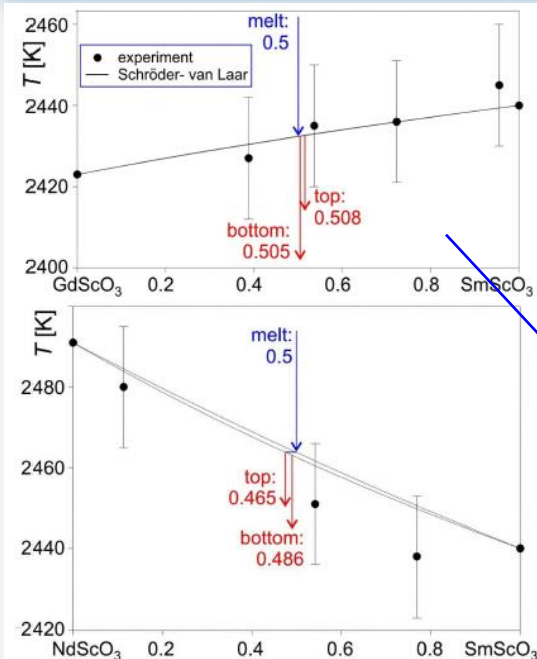


Fig. 4. Experimental phase diagrams GdScO_3 - SmScO_3 (top) and NdScO_3 - SmScO_3 (bottom) as derived from DTA melting peak onsets compared with theoretical liquidus and solidus curves calculated from T_f and ΔH_f . The arrow labels refer to the crystal growth data in Table III.

J.M. Badie, *Rev. Int. Hautes Temp. Réfract.*,
Fr. 15 (1978) 183-199.

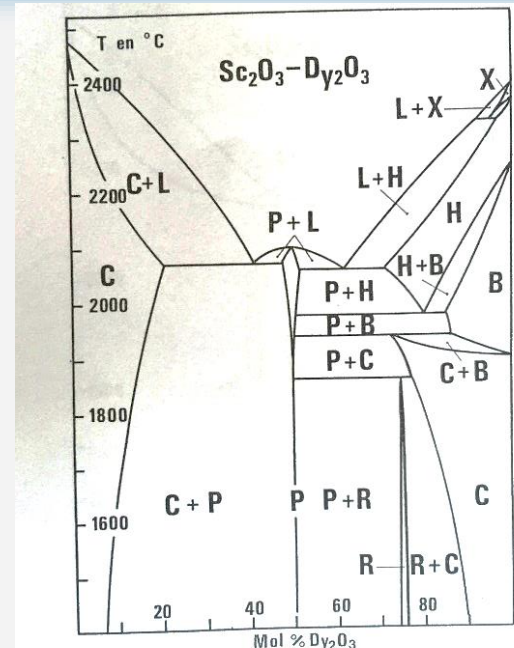
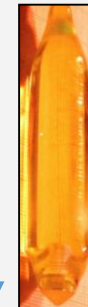
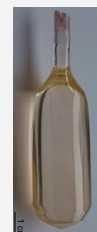


FIG. 10. - Diagramme de phases proposé compatible avec le polymorphisme de Dy_2O_3 .
FIG. 10. - Proposed phase diagram compatible with Dy_2O_3 polymorphism.

too hot

not existing, high pressure, or
incongruent



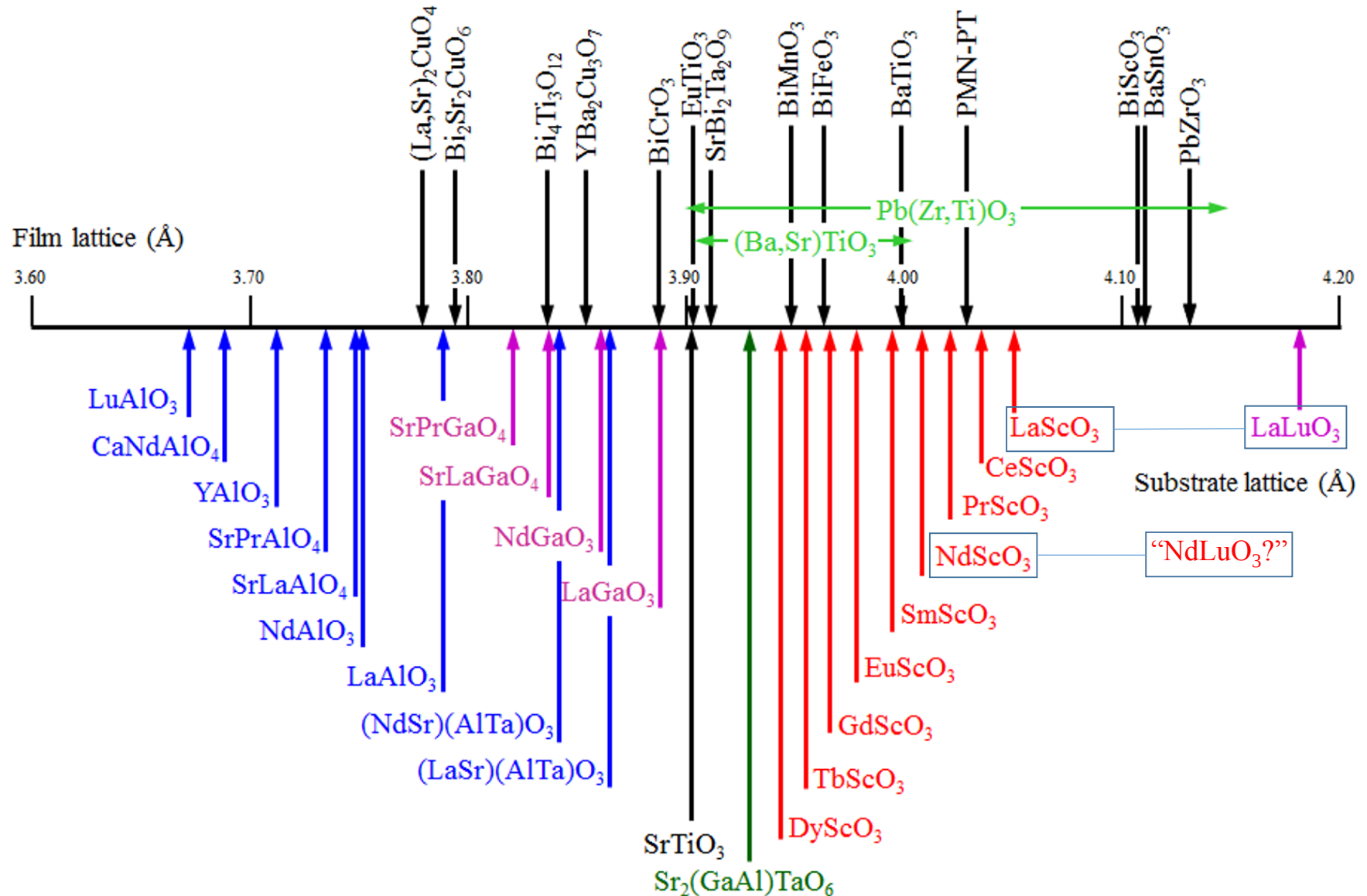
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.91	140.12	140.91	144.24	144.91	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.05	174.97
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium

?

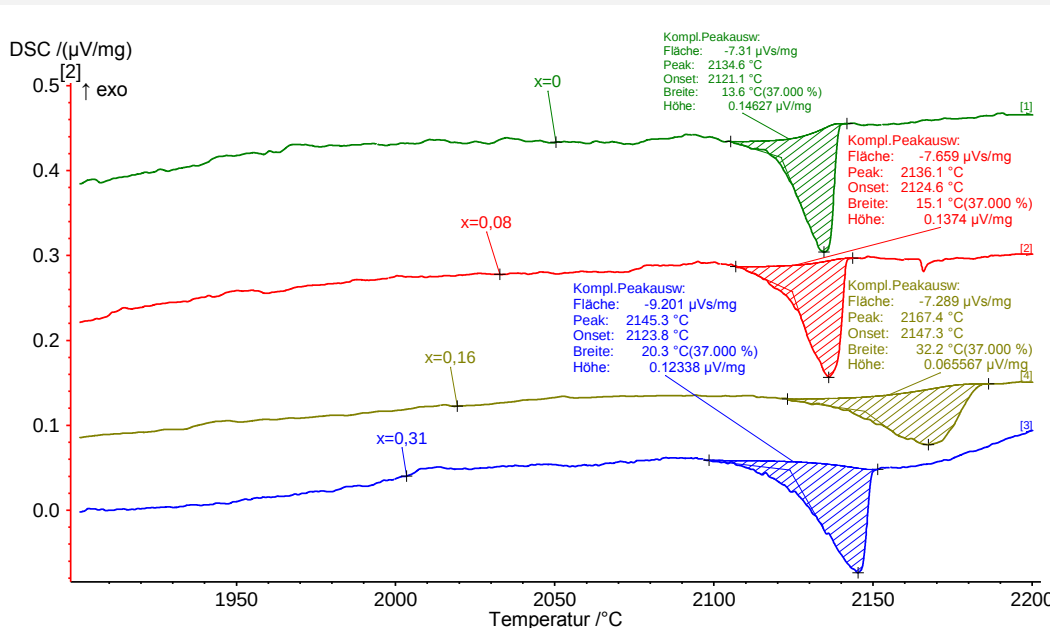
REScO_3 more stable
melting point rises
 a_{pc} rises

4.02 Å

3.95 Å

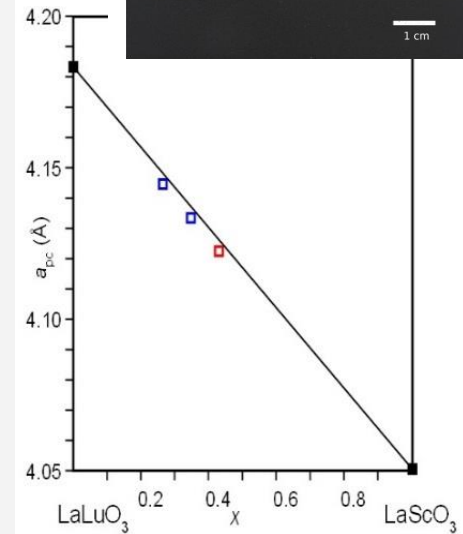
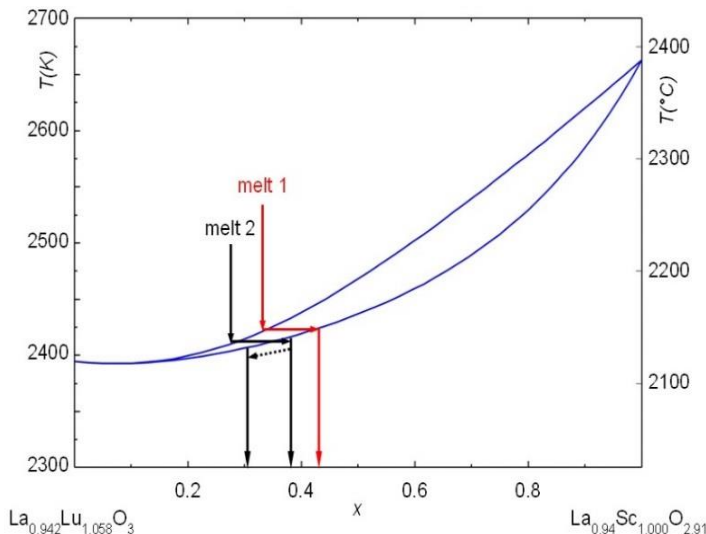
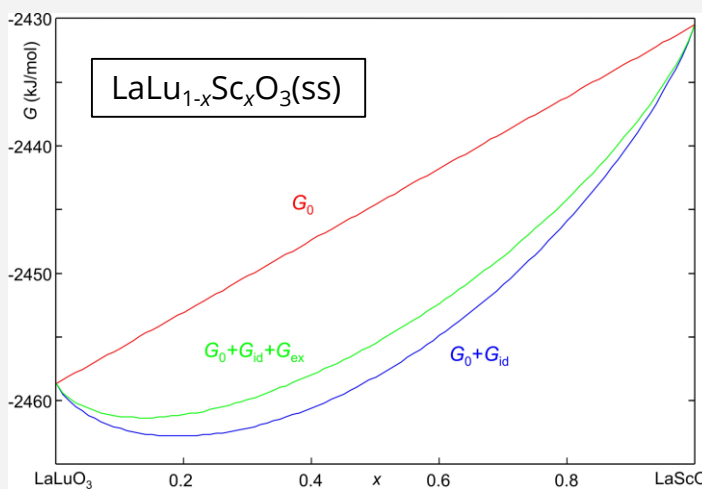
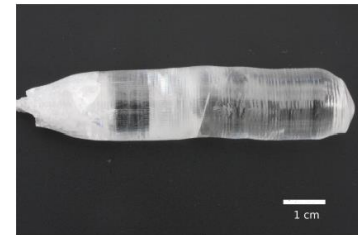


→ except LuAlO_3 , CeScO_3 and LaScO_3 all crystals are grown at IKZ.



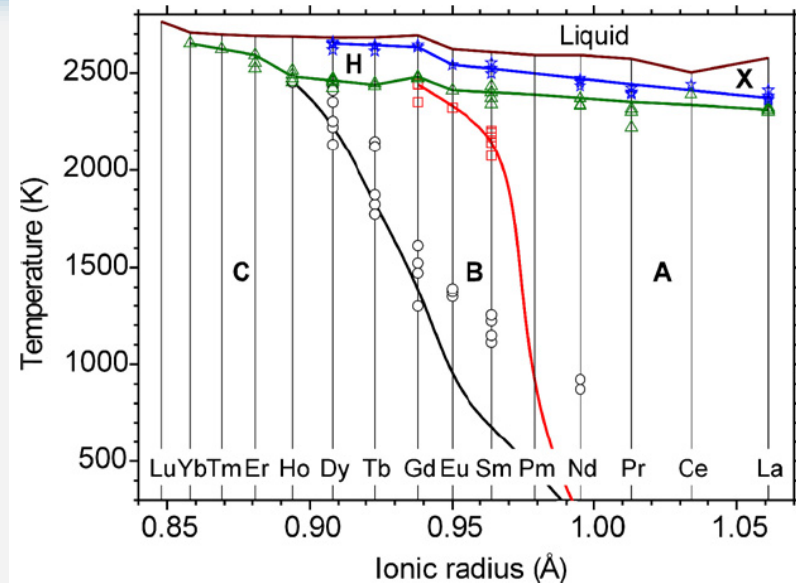
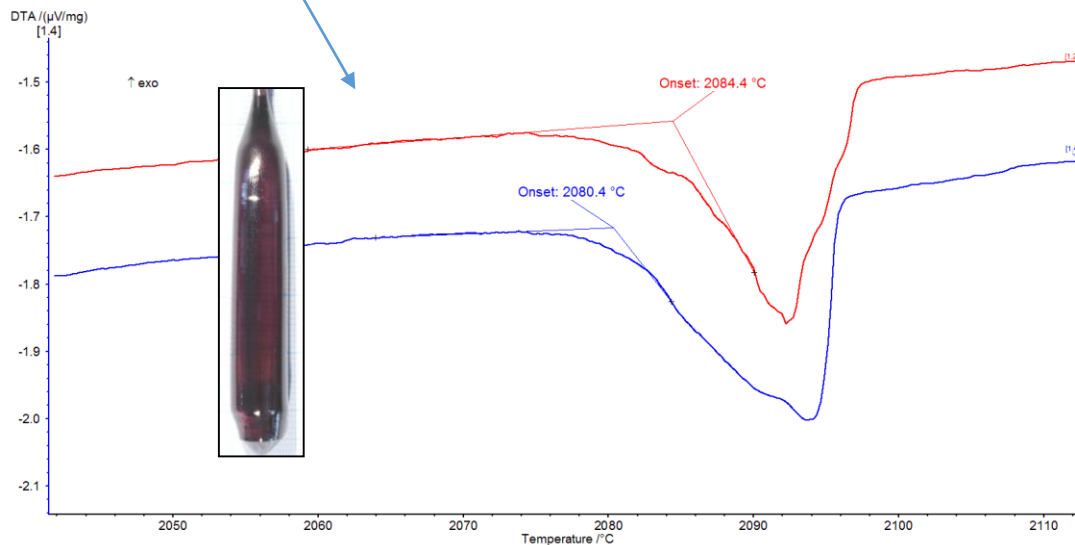
- DTA with STA 429CD (W furnace, lidded W crucible, static He atmosphere 6N purity)
 - Annealed powder samples, starting with $x = 0$ (LaLuO_3) towards LaScO_3 .
 - Melt onset rises not before $x \approx 0.4$ significantly.
 - The pseudobinary system is almost ideal.
 - Thermodynamic assessment:
Only for the solid phase (solid solution)
 $G(\text{ss}) = G_0 + G_{\text{id}} + G_{\text{ex}}$
a small contribution
 $G_{\text{ex}} = x(1-x)A$
($A = 10.9 \text{ kJ/mol}$) needed.
- 

LaLuO₃ – LaScO₃

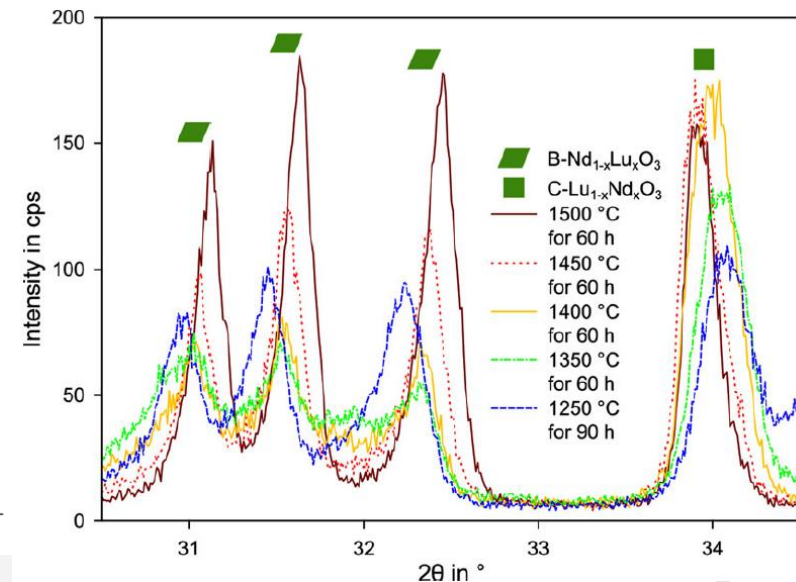


"NdLuO₃"

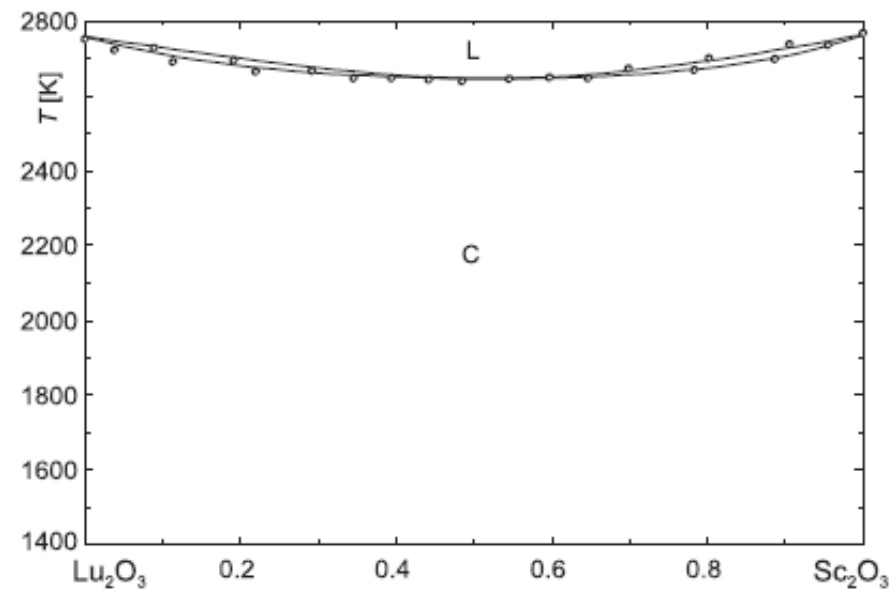
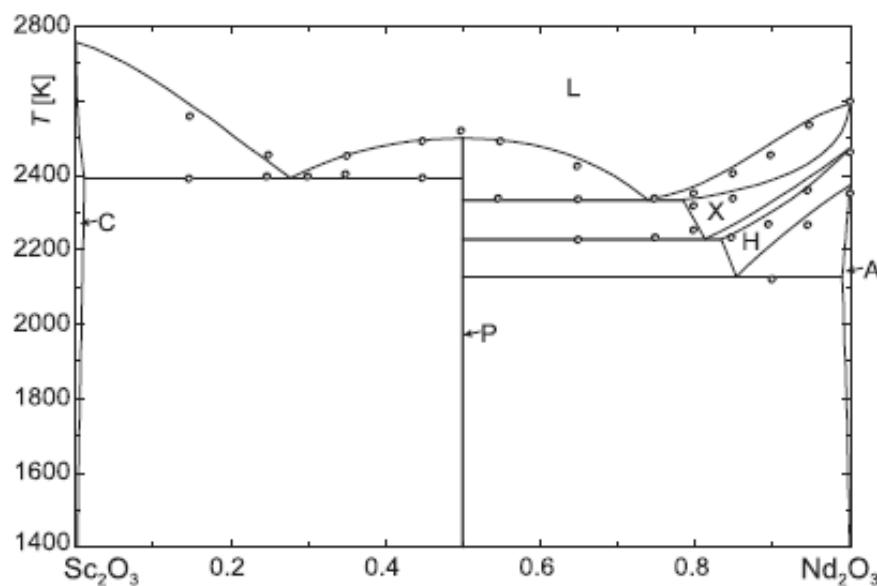
- The existence of P type NdLuO₃ is discussed controversially in the literature.
- Pure Lu₂O₃ is C-type, pure Nd₂O₃ is A-type.
- Annealed powders with nominal composition NdLuO₃ are mixtures of Lu-rich C-type and Nd-rich B-type Nd_{1-x}Lu_xO₃ phases.
- (cf. Hirsch et al., *Cryst. Res. Technol.* 52 (2017) 1600237).
- But: NdScO₃ is stable!**



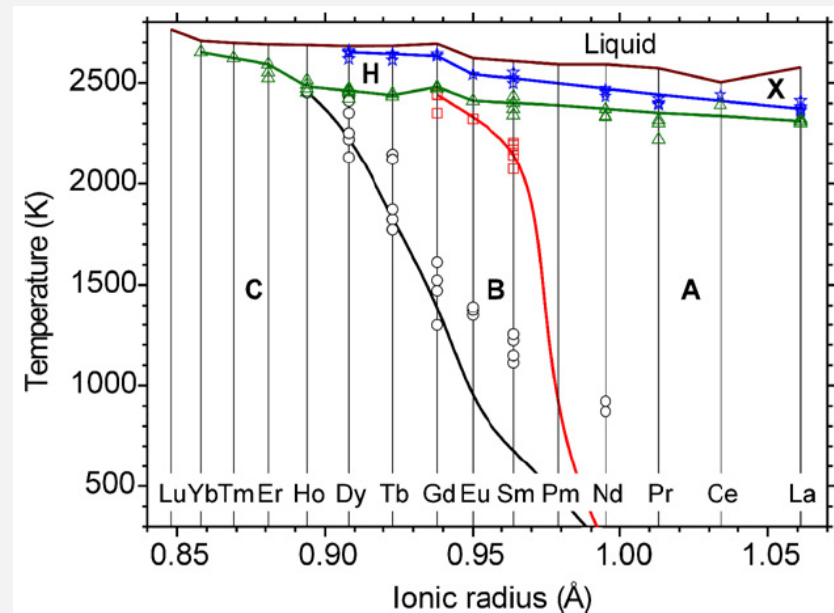
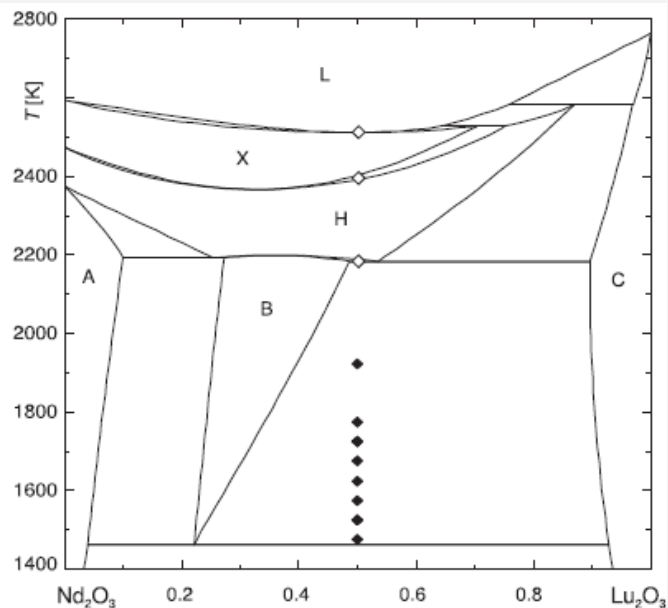
Polymorphism of the rare-earth sesquioxides:
Zinkevich, *Prog. Mat. Sci.* 52 (2007) 597-647.

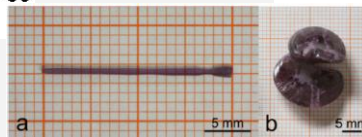
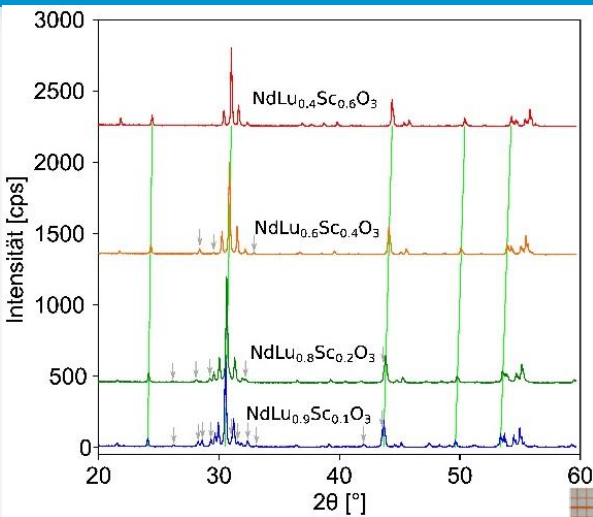


Annealed 1:1 mixture Nd₂O₃:Lu₂O₃ contains C + B.



Experimental results of Badie for the Nd_2O_3 - Sc_2O_3 and Lu_2O_3 - Sc_2O_3 systems and a FactSage thermodynamic assessment. (cf. Hirsch et al., *J. Crystal Growth* 505 (2019) 38-43.)



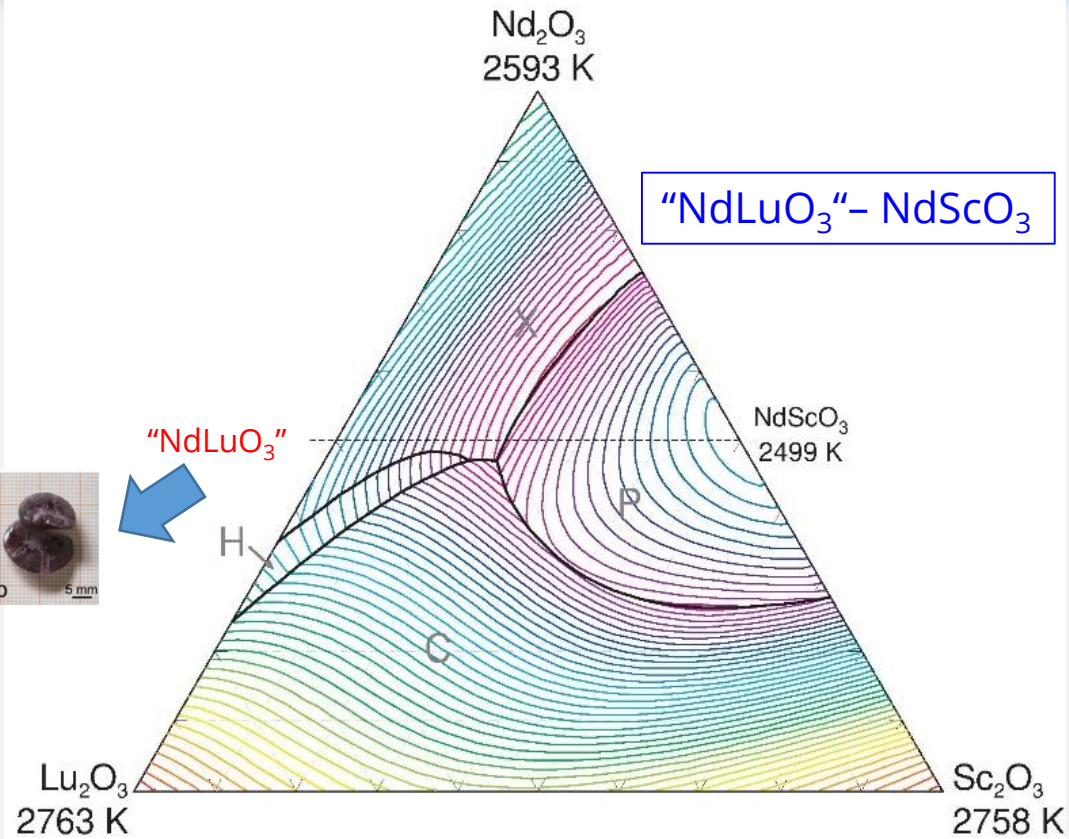
NdLu_{0.15}Sc_{0.85}O₃

Binary interactions:

$$G_{\text{ex}}^{\alpha,\beta} = {}^0Lx_{\alpha}x_{\beta} + {}^1Lx_{\alpha}x_{\beta}(x_{\alpha}-x_{\beta}) + {}^2Lx_{\alpha}x_{\beta}(x_{\alpha}-x_{\beta})^2$$

Ternary interactions:

$$G_{\text{ex}}^{\alpha,\beta,\gamma} = {}^0Lx_{\alpha}x_{\beta}x_{\gamma}$$



Phase	Nd ₂ O ₃ -Lu ₂ O ₃		Nd ₂ O ₃ -Sc ₂ O ₃		Lu ₂ O ₃ -Sc ₂ O ₃		Nd ₂ O ₃ -Lu ₂ O ₃ -Sc ₂ O ₃		Nd ₂ O ₃ -Sc ₂ O ₃	
	0L		1L		2L					
C	27000	20000	15000	20000	-	-				
B	10500	0	0	20000	-	-				
A	20900	-10000	0	0	-	-				
H	17200	-37000	15995	20000	-	-				
X	12600	-48000	12850	0	-	-				
L	0	-80000	0	-30000	-17000	-30000				

Summary

1. Experimental thermal analysis at very high $T > 2000^\circ\text{C}$ is often a challenge. But fortunately, the theoretical description is often not very difficult, because many phases approach ideal behavior.
2. Missing Gibbs free energy data can often be estimated from data of isostructural phases (e.g., garnets).
3. The mutual solubility of RE based perovskite and garnet phases is often high – enabling tuning of structural and physical properties.

4. Thank you for your attention!

