Oxide Structures Containing Sodium Cations in Trigonal Prismatic Environments

Hanno zur Loye

Department of Chemistry and Biochemistry
University of South Carolina, Columbia, SC 29208

Oxides and Trigonal Prismatic Sites

- In oxides, octahedral coordination is "typical" - while trigonal prismatic coordination "atypical"
- Close-packed structures generate octahedral sites Some examples in the literature:
  - Monoclinic $Na_{0.42}CoO_2$
    Takada et al. Chem. Mater. 17 (2005) 2034
  - Hexagonal $Li_{0.43}Na_{0.36}CoO_{1.96}$
    Balsys et al. Solid State Ionics 69 (1994) 69
- AA stacking generates trigonal prismatic sites - e.g. MoS_2

Single Crystal Synthesis

Flux Growth - the use of a high temperature melt of an inorganic compound as the solvent for crystallization

Qualities of an Ideal Flux

1. High solubility of constituents
2. Low melting point
3. Low volatility
4. Low reaction with the container
5. Absence of incorporation into the structure
6. Readily available
7. Ease of separation after synthesis
8. Low toxicity

Potential Fluxes

PbO

KF

NaCl/KCl

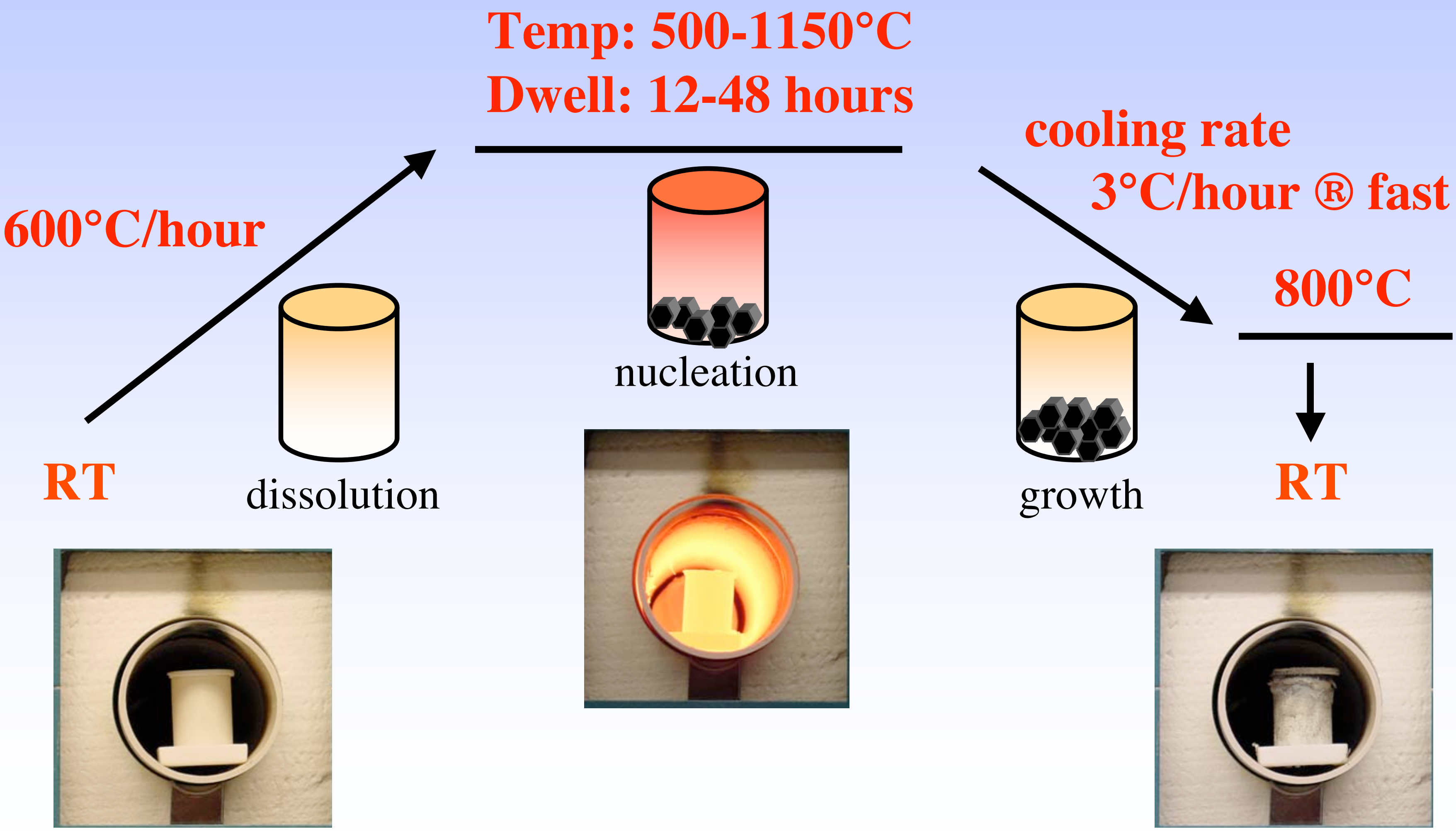
KOH/NaOH

Na_2CO_3

K_2CO_3

Elwell, D; Scheel, H.J. *Crystal Growth from High-Temperature Solutions;* Academic Press: New York, 1975.

Flux Synthesis



Changing the Melt Composition

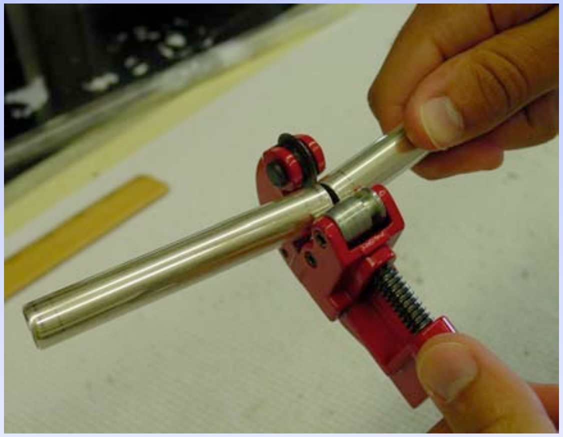
- Acid/Base Chemistry of Hydroxide Melts
  - Water: $2H_2O \leftrightarrow H_3O^+ (aq) + OH^- (aq)$

    Hydroxide melt: $2OH^- \leftrightarrow H_2O (sol) + O^{2-} (sol)$

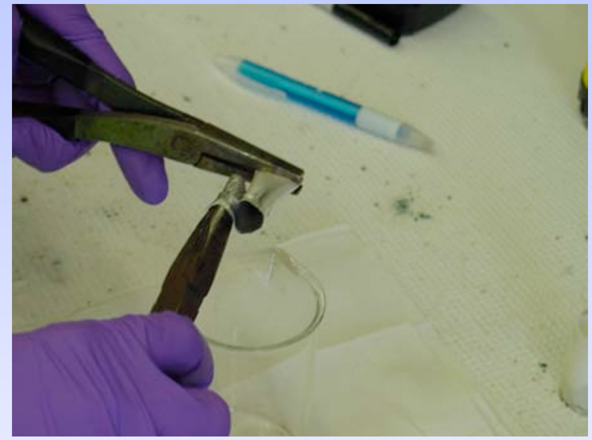
- "Wet" Melt Preparation
  - Add 2g H_2O and seal in silver tube

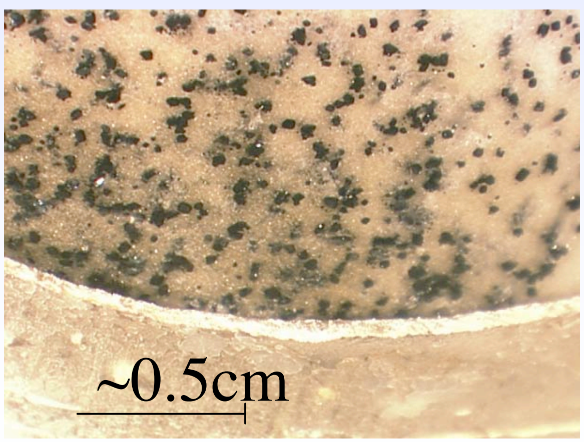
- "Dry" Melt Preparation
  - Use open crucible and heat slowly (1°C/min)

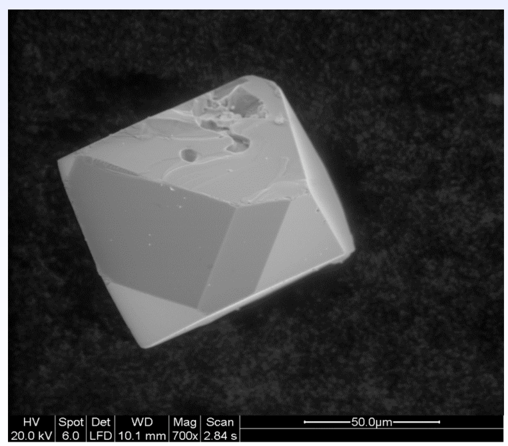
Single Crystal Growth

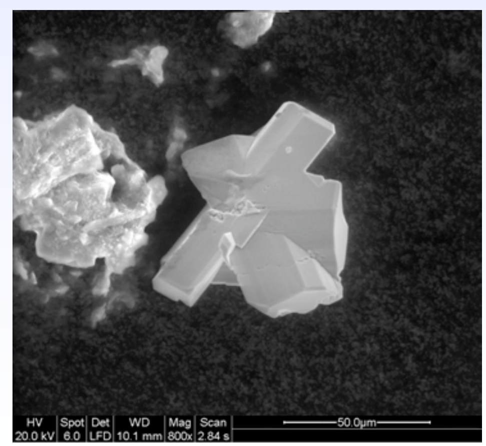


Single Crystal Growth



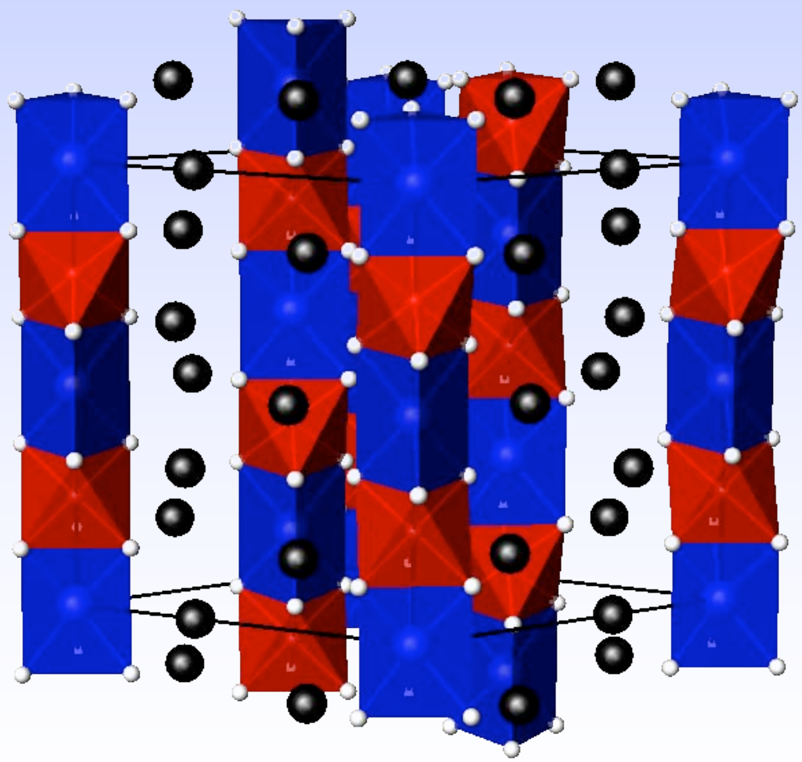


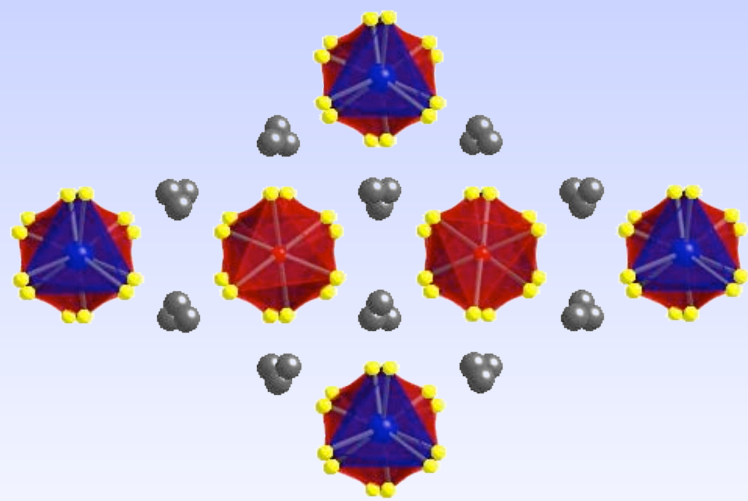




2H-Perovskite Related Structures: Sr_3NiPtO_6
Nickel in Trigonal Prismatic Coordination

Infinite chains of alternating octahedra and trigonal prisms. Platinum is in octahedral coordination while nickel is in a trigonal prismatic coordination environment.

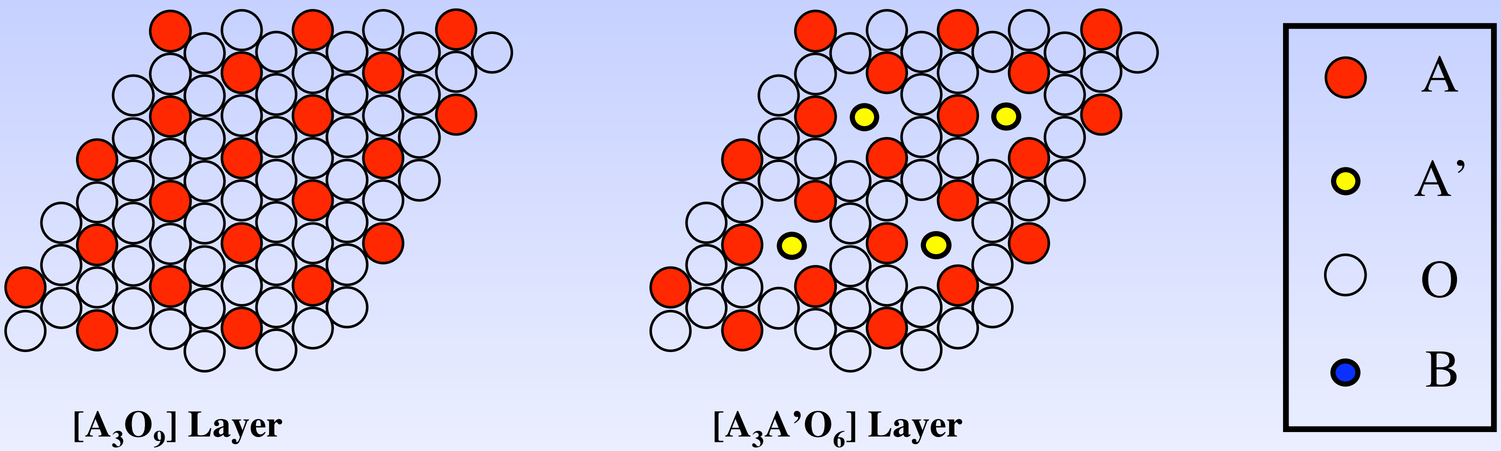




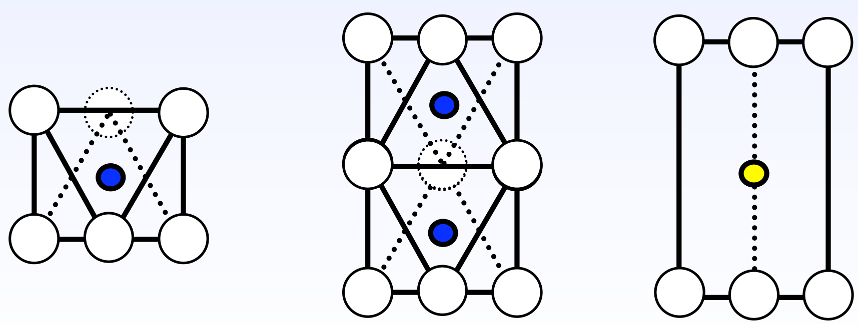
In oxide structures, it is easy to explain octahedral sites. It is very rare to observe a trigonal prismatic coordination environment. This has to do with the type of layers (AO_3) that stack to form oxide structures.

Nguyen, T., Giaquinta, D. M., zur Loye, H.-C., *Chem. Mater*. **1994**, *6*, 1642.

Stacking of Layers and Resulting Coordination Environments

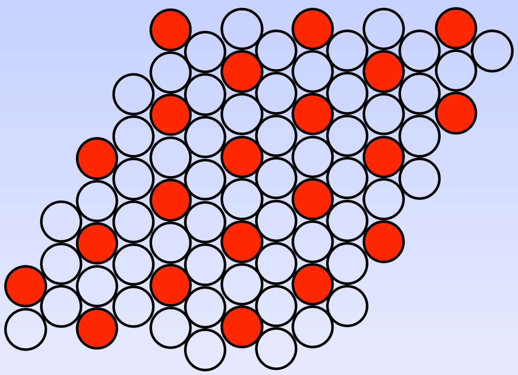


$[A_3O_9]$ Layer **$[A_3A'O_6]$ Layer**

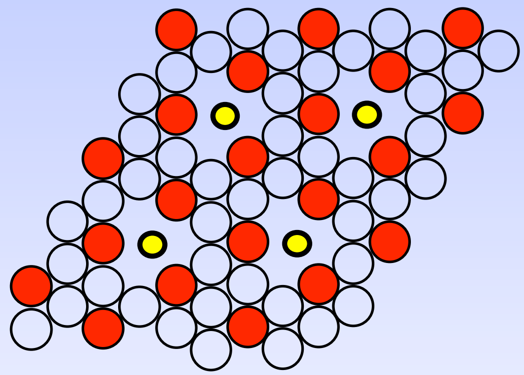


Darriet, J., Subramanian, M. *J. Mater. Chem.* **1995**, *5*, 543.
Perez-Mato, J.M.; Zakhour-Nakhl, M.; Weill, F.; Darriet, J. *J. Mater. Chem.* **1999**, *9*, 2795.

$A_{3n+3m}A'_nB_{n+3m}O_{6n+9m}$ Family of Structures
A' cation in Trigonal Prismatic Coordination



$[A_3O_9]$ Layer



$[A_3A'O_6]$ Layer

A = Mg, Ca, Sr, Ba

A' = Li, Na, Co, Ni, Cu, Zn, Ca, Sr, Ba, Mg, RE

O

B **Pt, Ir, Ru, Rh, Ni**

Stacking *n* $[A_3A'O_6]$ layers with *m* $[A_3O_9]$ layers

→ $A_{3n+3m}A'_nB_{n+3m}O_{6n+9m}$

Darriet, J., Subramanian, M. *J. Mater. Chem.* **1995**, *5*, 543.
Perez-Mato, J.M.; Zakhour-Nakhl, M.; Weill, F.; Darriet, J. *J. Mater. Chem.* **1999**, *9*, 2795.

Crystal growth of $(Ln_2Na)NaPtO_6$ (Ln = La, Nd) Sodium in Trigonal Prismatic Coordination

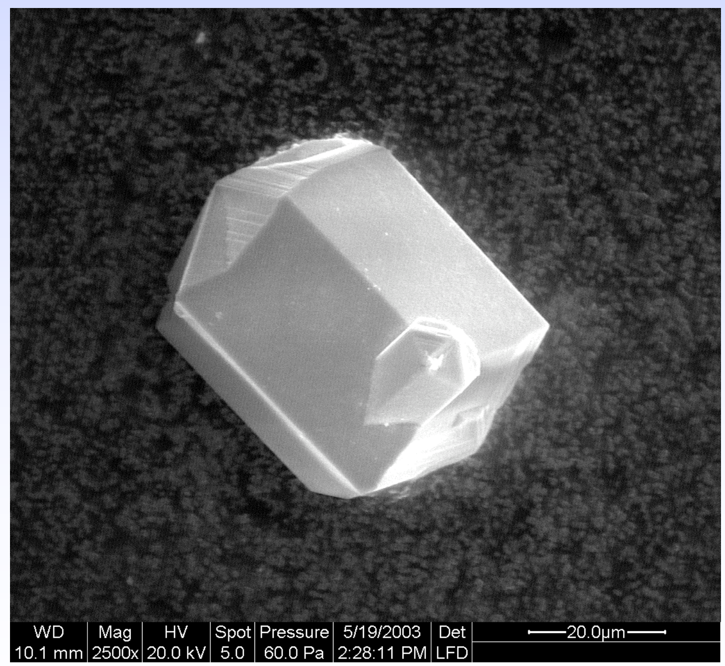
2 g H_2O

$$Ln_2O_3 + (NH_4)_2PtCl_6 + NaOH \xrightarrow[\text{Ag crucible}]{700\ °C,\ 12\ hr} (NaLn_2)NaPtO_6$$

First example of an $A_3A'BO_6$ oxide with more than one metal on the A-site AND a something other than Ca, Sr, Ba on the A-site.

R-3c
a = 9.5031(2) Å
c = 11.4625(5)
R1 = 2.38%
wR2 = 4.59%

Na(CN6) 1.02
Na(CN8) 1.18
Na(CN9) 1.24
La(CN8) 1.16

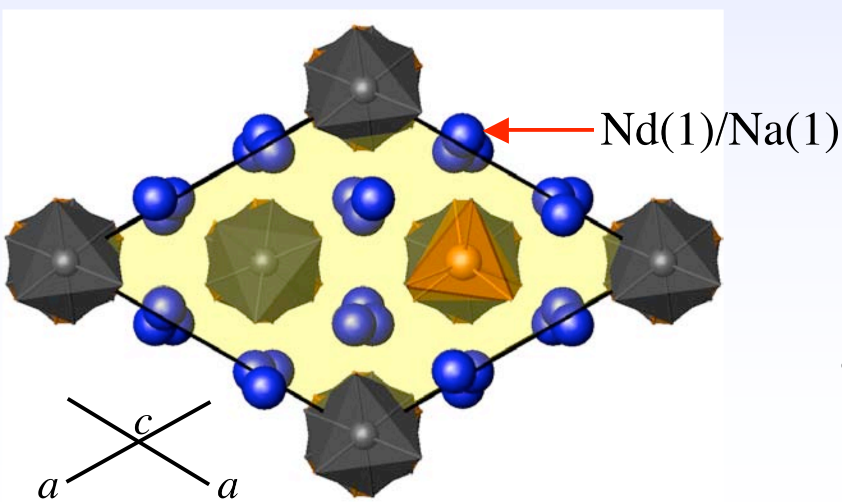


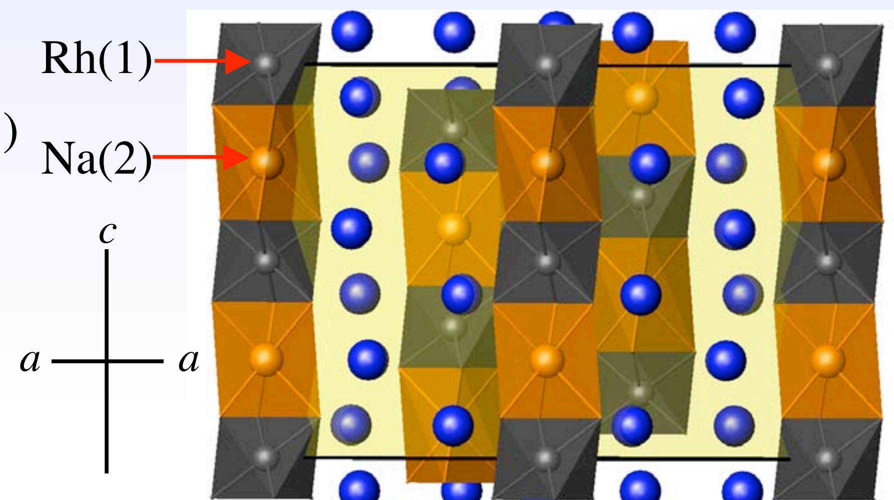
Davis, M.J.; Smith, M.D.; zur Loye, H.-C. *Inorg. Chem.* **2003**, *42*, 6980.

Crystal growth of $(Ln_{2.5}Na_{0.5})NaRhO_6$ (Ln = La, Pr, Nd)
Sodium in Trigonal Prismatic Coordination

$$Ln_2O_3 + Rh° + Na_2CO_3 \xrightarrow[Al_2O_3\ \text{crucible}]{1050\ °C,\ 36\ hrs} (Ln_{2.5}Na_{0.5})NaRhO_6$$

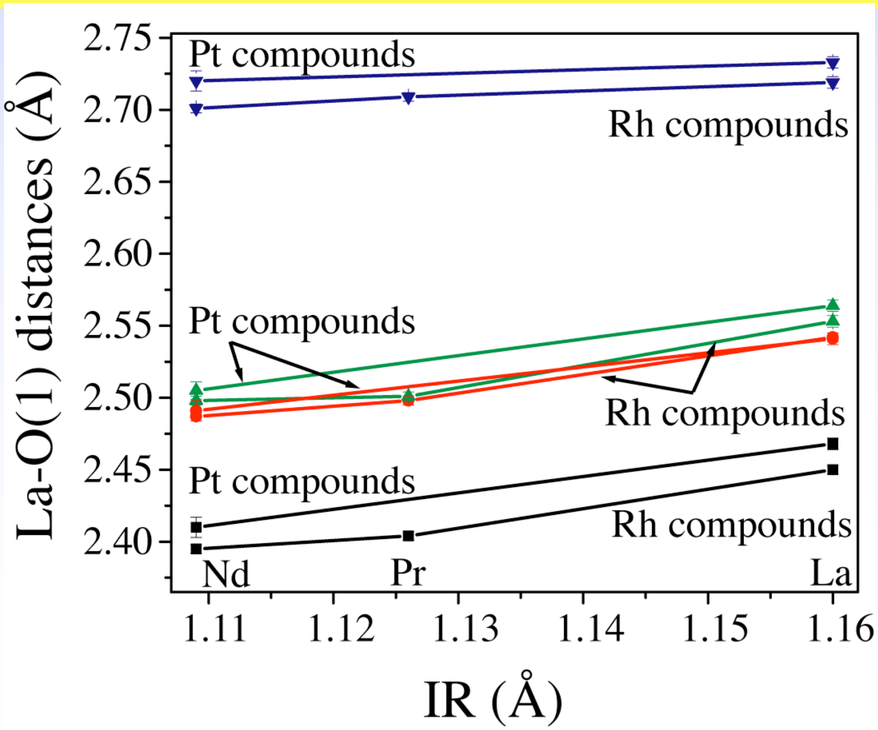
Ln(1)/Na(1) in an 8-coordinate environment. Rh(1) in octahedral coordination, Na(2) in distorted trigonal prismatic coordination.

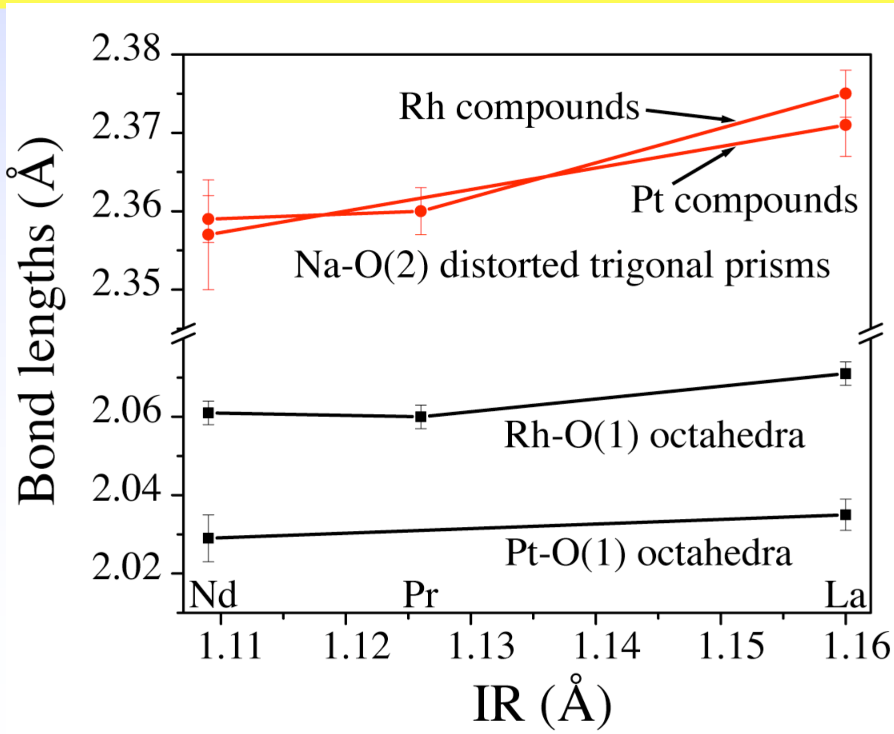




$(A_{3\text{-}x}A'_x)A'MO_6$
(A = La, Nd, Pr; A' = Na; M = Rh(III), Pt(IV))

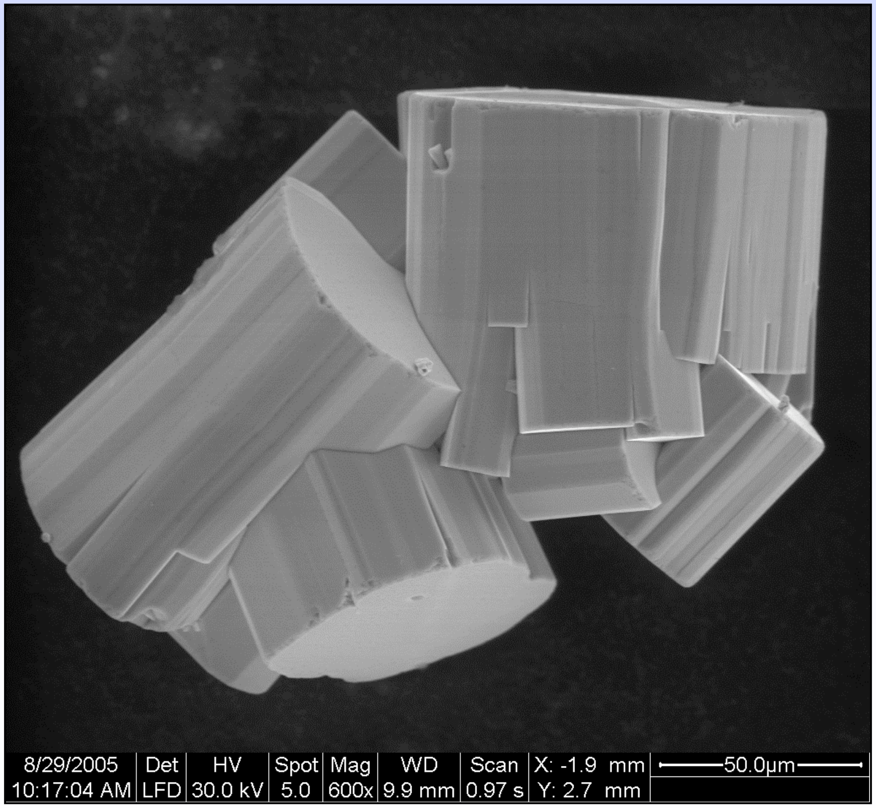
	$(La_{2.47}Na_{0.53})NaRhO_6$	$(Pr_{2.45}Na_{0.55})NaRhO_6$	$(Nd_{2.46}Na_{0.54})NaRhO_6$	$La_{2.22}NaPtO_6$	$(Nd_2Na)NaPtO_6$
A-O(1) x 2	2.450(3)	2.404(3)	2.395(3)	2.468(4)	2.410(7)
A-O(1) x 2	2.542(3)	2.498(3)	2.487(3)	2.541(4)	2.491(7)
A-O(1) x 2	2.553(4)	2.501(3)	2.498(3)	2.564(4)	2.505(6)
A-O(1) x 2	2.719(4)	2.709(3)	2.701(3)	2.733(4)	2.720(7)
M(1)-O(1) x 6	2.071(3)	2.060(3)	2.061(3)	2.035(4)	2.029(6)
Na(2)-O(1) x 6	2.375(3)	2.360(3)	2.359(3)	2.371(4)	2.357(7)

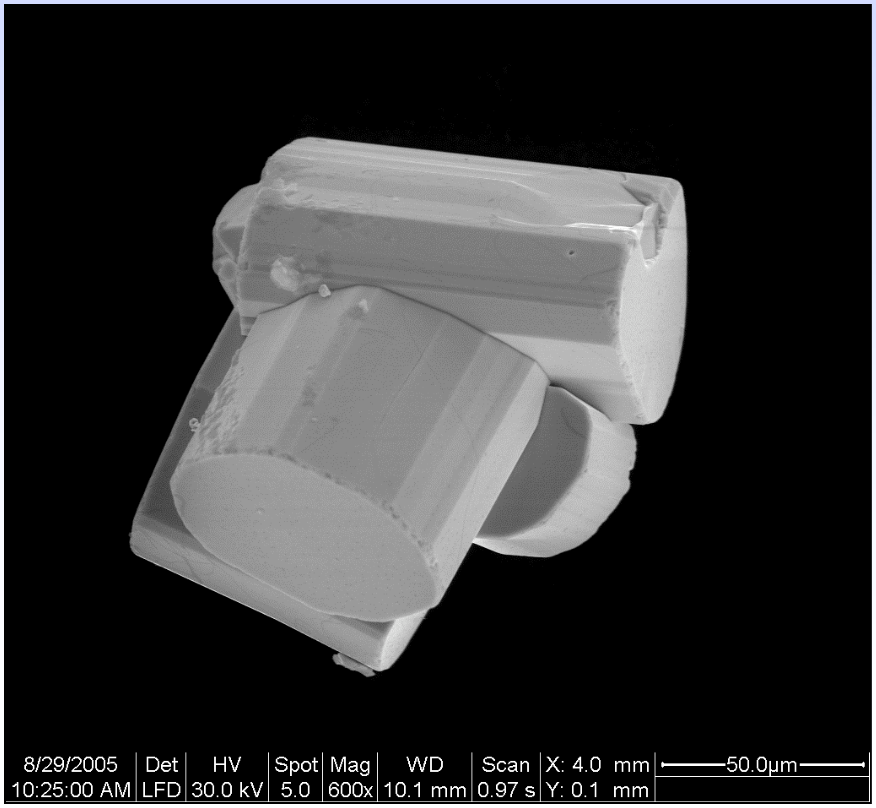




Synthesis of *Ln*NaIrO$_4$ (Ln = Gd - Er, Y)

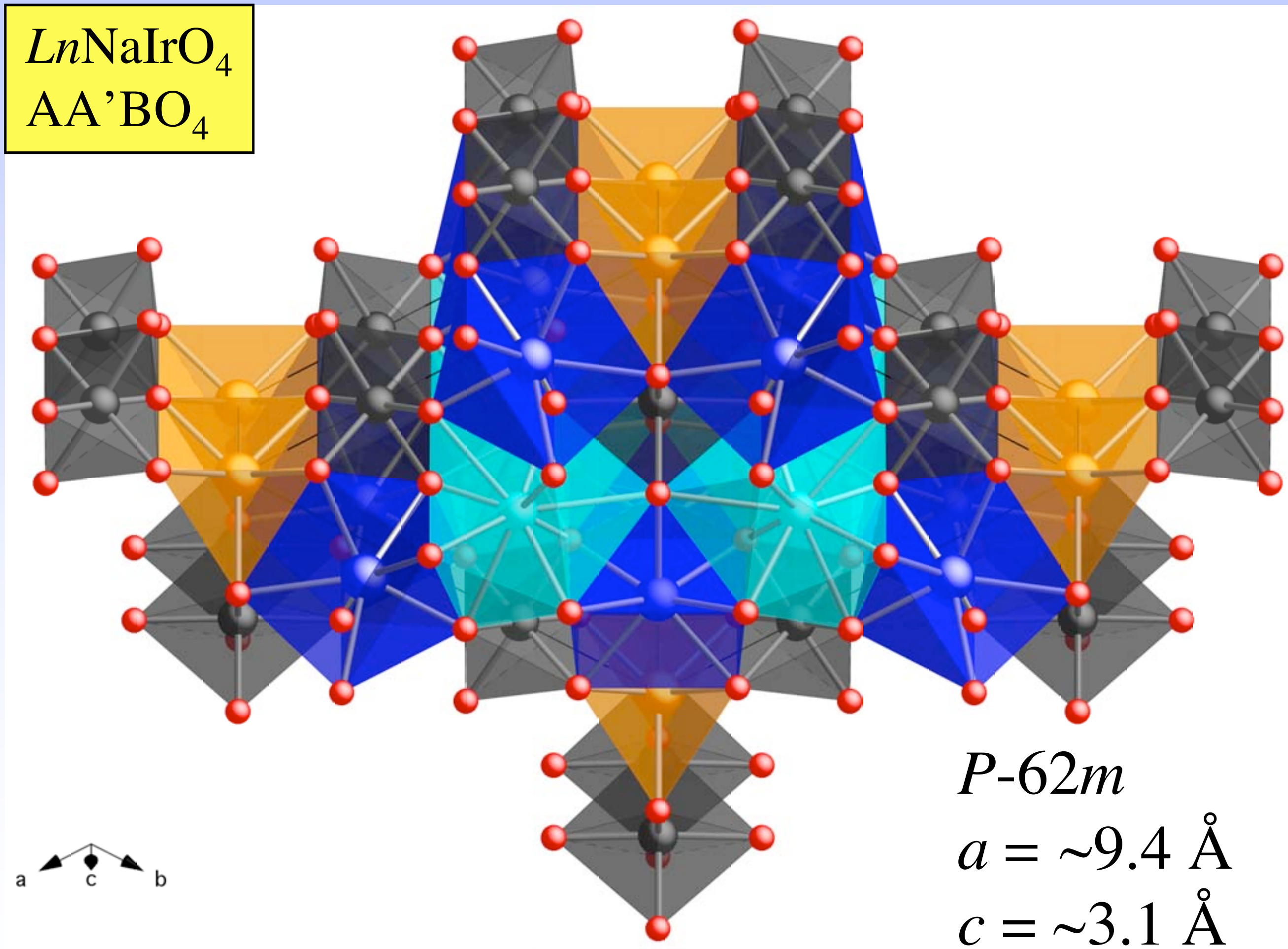
$$Ln_2O_3 + Ir + NaOH/CsOH \xrightarrow[\text{Ag tube}]{650\ ^\circ C,\ 24\ hr} LnNaIrO_4$$





Structure of LnNaIrO$_4$ (Ln = Gd - Er, Y)
Sodium in Trigonal Prismatic Coordination

*Ln*NaIrO$_4$
AA'BO$_4$



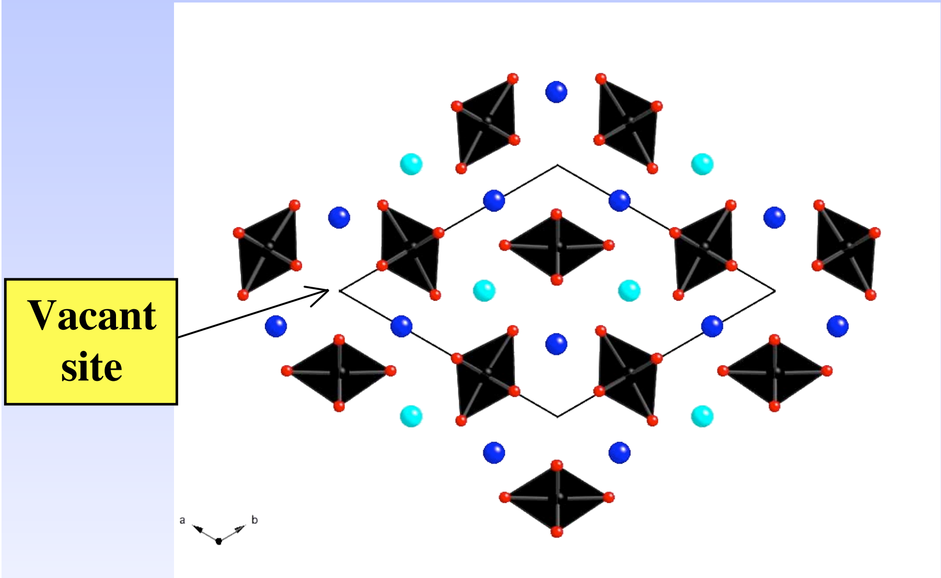
Ir^{4+} = black
Na(1) = orange
Ln(1) = light blue
Ln(2)/Na(2) = blue
O = red

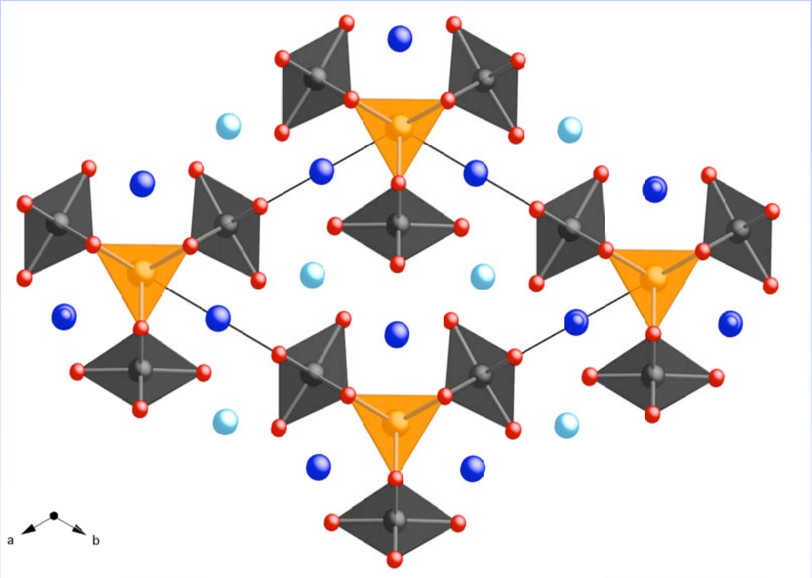
Structure related to that of Ca$_{2-x}$IrO$_4$[1]

P-62*m*
a = ~9.4 Å
c = ~3.1 Å

[1]Dijksma et. al. *Mat. Res. Bull*. 28, **1993**, 1145.

Structure of $Ca_5Ir_3O_{12}$ ($Ca_{2-x}IrO_4$) vs. $LnNaIrO_4$*





Edge sharing IrO_6 octahedra

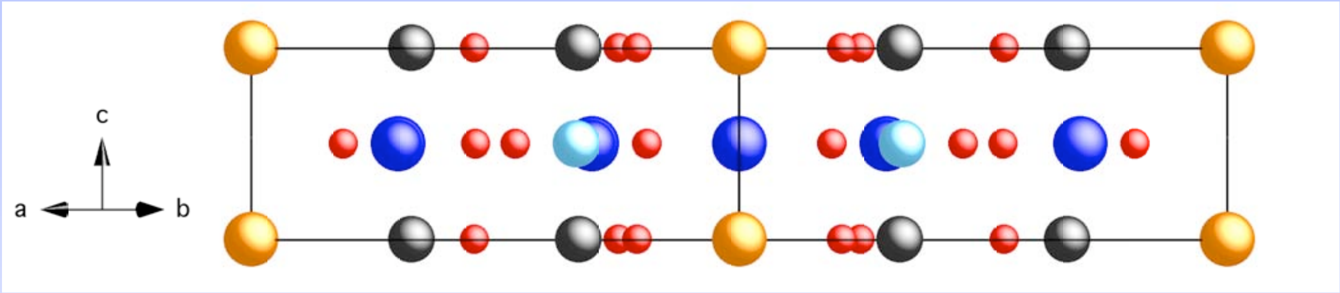
Edge sharing IrO_6 octahedra and face-sharing NaO_6 trigonal prisms.

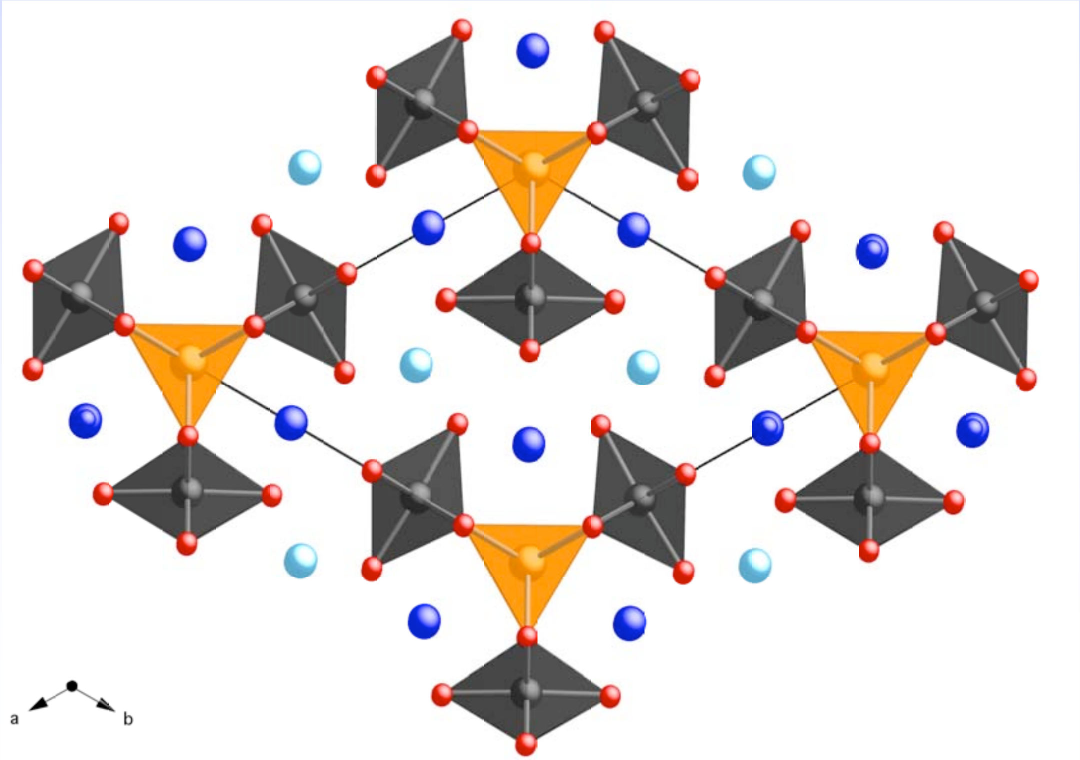
The vacant sites in the $Ca_5Ir_3O_{12}$ structure are filled by sodium cations in the $LnNaIrO_4$ structure.

* Wakeshima, M.; Taira, N.; Hinatsu, Y.; Ishii, Y. *Solid State Comm*. **2003**, *125*, 311.

* Dijksma, F. J. J.; Vente, J. F.; Frikkee, E.; Ijdo, D. J. W. *Mat. Res. Bull*. **1993**, *28*, 1145.

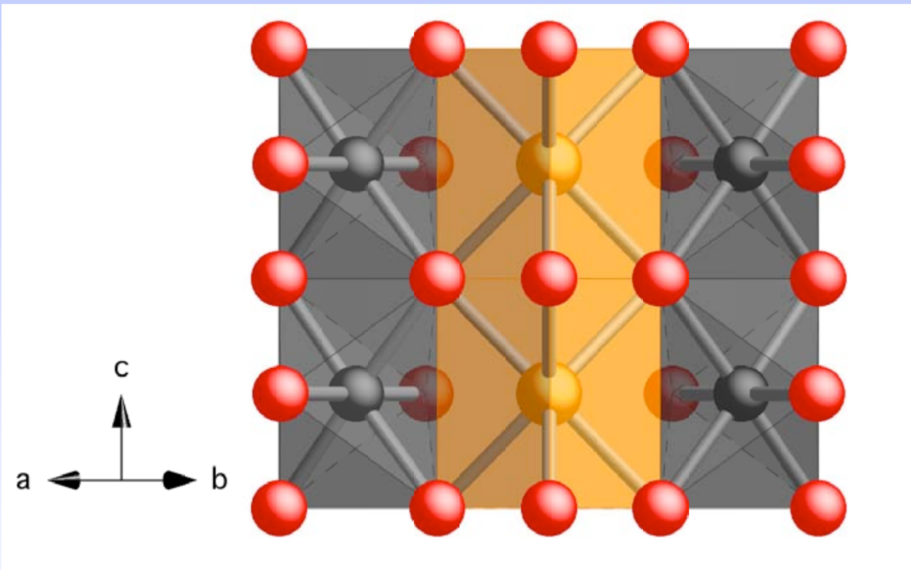
Structure of $LnNaIrO_4$

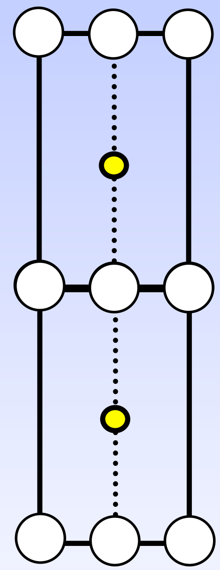




Ir^{4+} = black
Na(1) = orange
Ln(1) = light blue
Ln(2)/Na(2) = blue
O = red

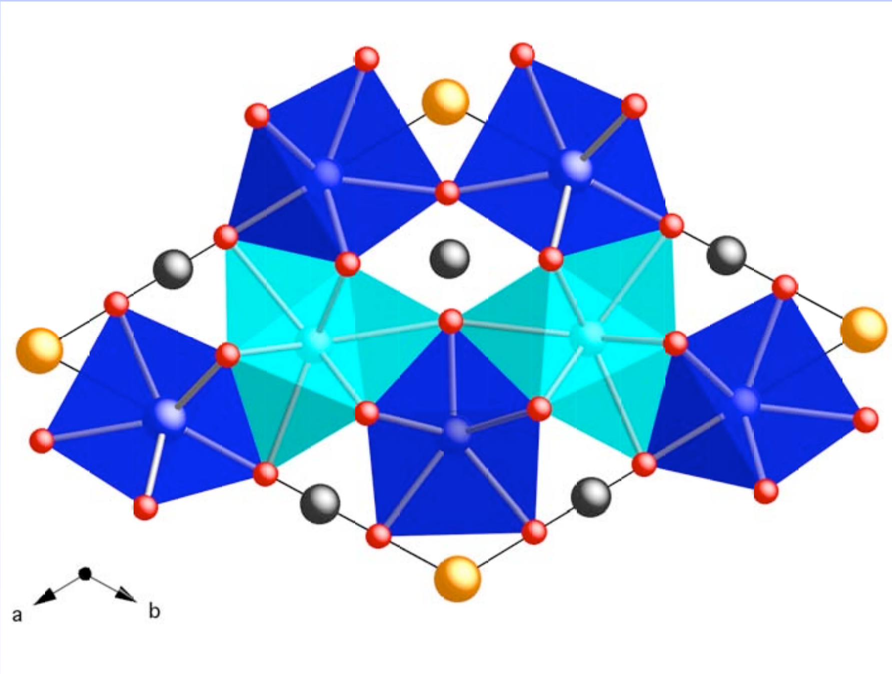
Arrangement of the IrO_6 - Octahedra and NaO_6 - Trigonal Prisms in $LnNaIrO_4$

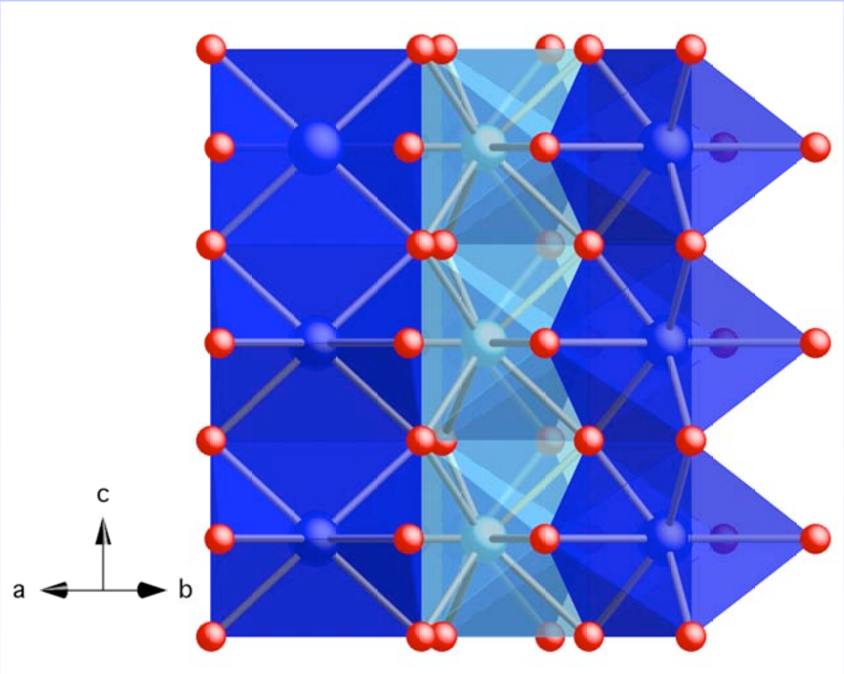




Infinite chains of face-sharing NaO_6 trigonal prism share edges with infinite chains of edge-sharing IrO_6 octahedra. The chains run down the c-axis

Structure of LnNaIrO$_4$



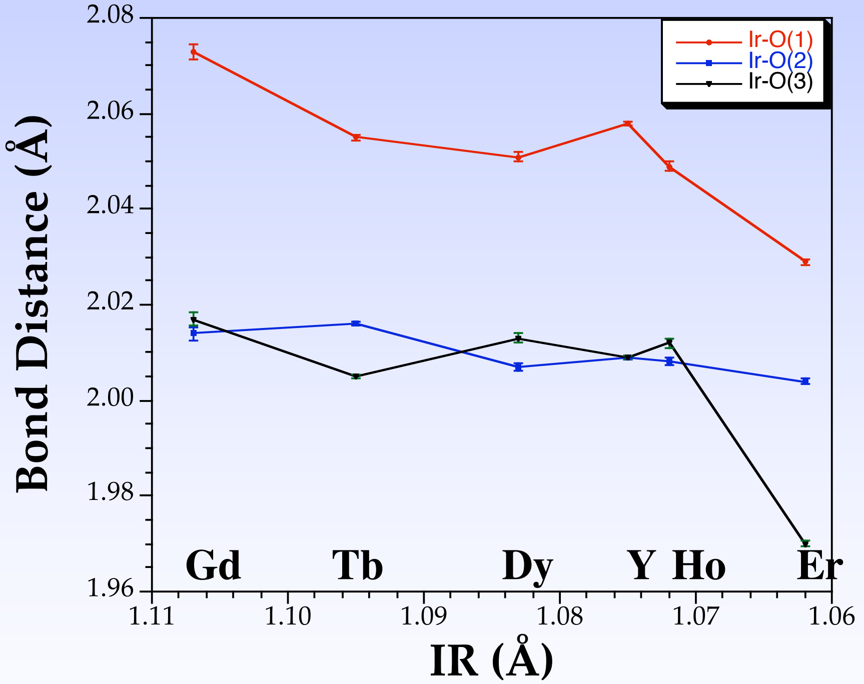


Dark blue - (*Ln*/Na)O$_7$ capped-trigonal prisms Occupancy:1/3 *Ln*(2), 2/3 Na(2)
Light blue - *Ln(1)* distorted tri-capped trigonal prisms

Oxidation State of Iridium in $Ln_{1-x}Na_{1+x}IrO_4$ (Ln = Gd - Er, Y)

Ir-O bond distances as a function of CN = 9 rare earth ionic radius

The sodium content varies and increases (at the expense of the rare earth content) with decreasing size of the rare earth. This directly impacts the oxidation state of the iridium and should be reflected in the size of the IrO_6 octahedra.

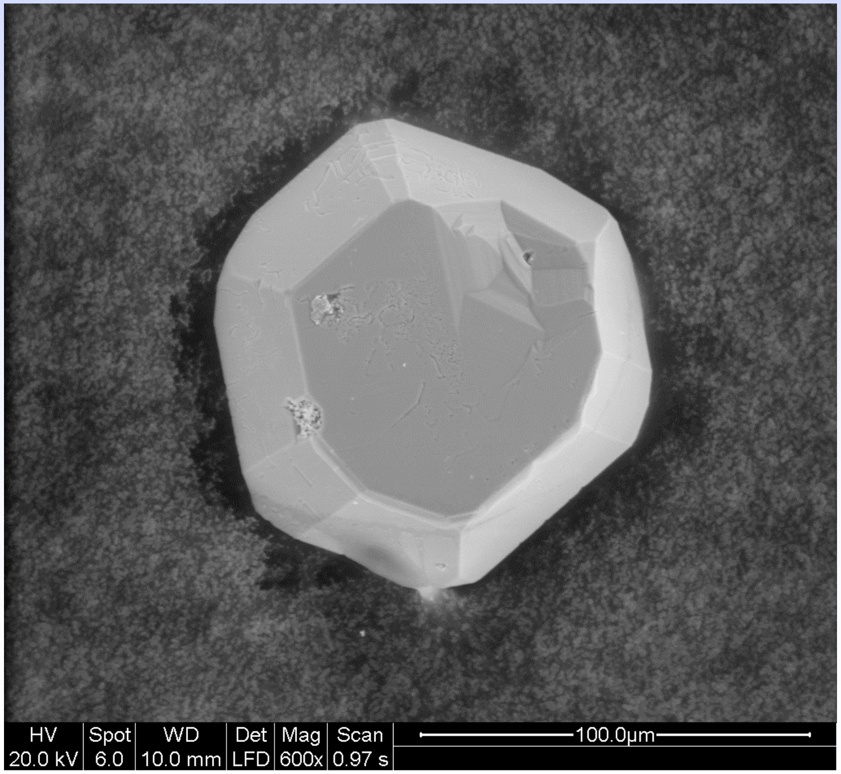


Based on single crystal X-ray diffraction data

Rare Earth	Gd	Tb	Dy	Y	Ho	Er
Na-Content	1.04	1.07	1.06	1.08	1.10	1.26
Ir Oxidation State	4.08	4.14	4.12	4.16	4.20	4.52

Synthesis of $Ln_{14}Na_3Ru_6O_{36}$ Ln = Pr, Nd

$$Ln_2O_3 + RuO_2 \xrightarrow[\text{Ag tube, 600C 12h}]{\text{NaOH}} Ln_{14}Na_3Ru_6O_{36}$$



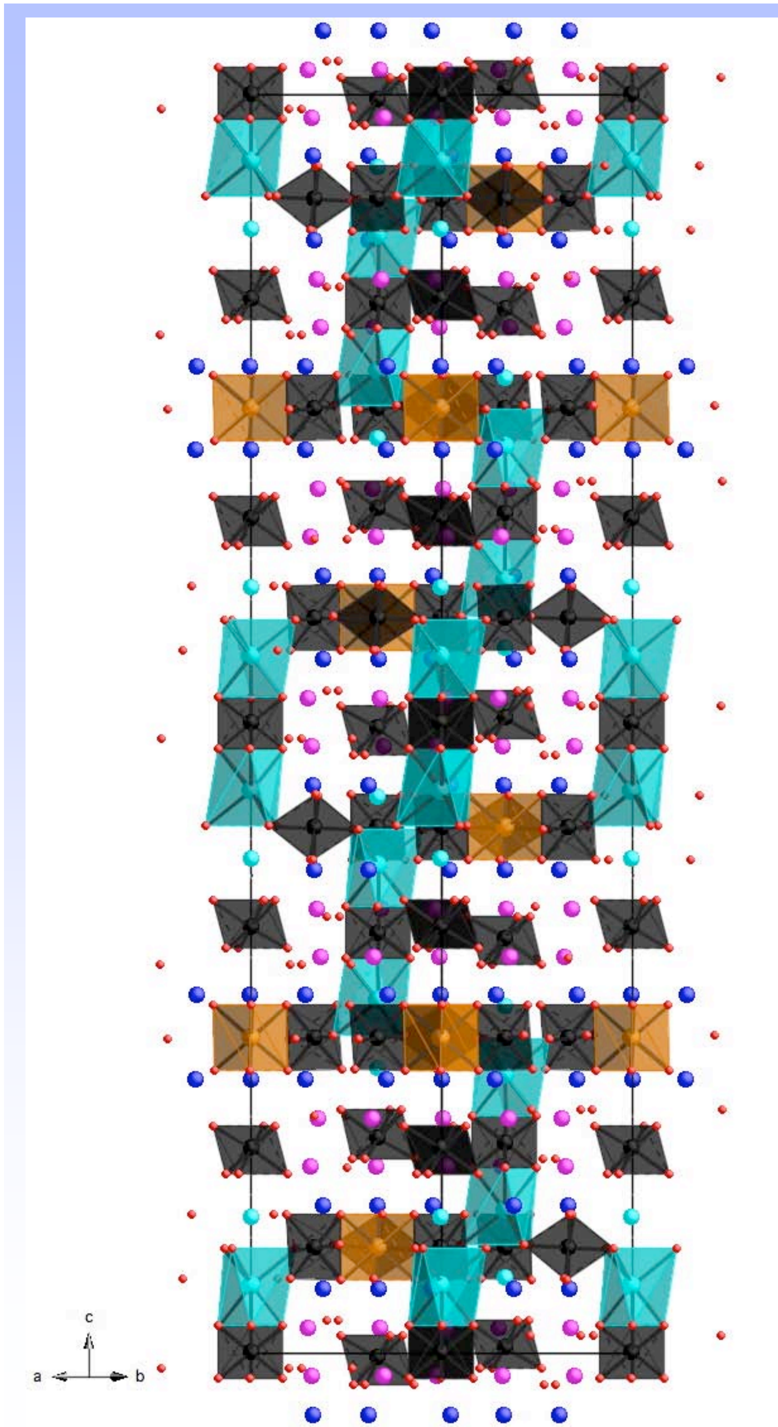
$Pr_{14}Na_3Ru_6O_{36}$

R-3c
a = 9.7380(2) Å
c = 55.5716(15)
R1 = 3.68 %
wR2 = 7.27 %

$Nd_{14}Na_3Ru_6O_{36}$

R-3c
a = 9.6781(2) Å
c = 55.4156(18)
R1 = 3.20 %
wR2 = 6.77 %

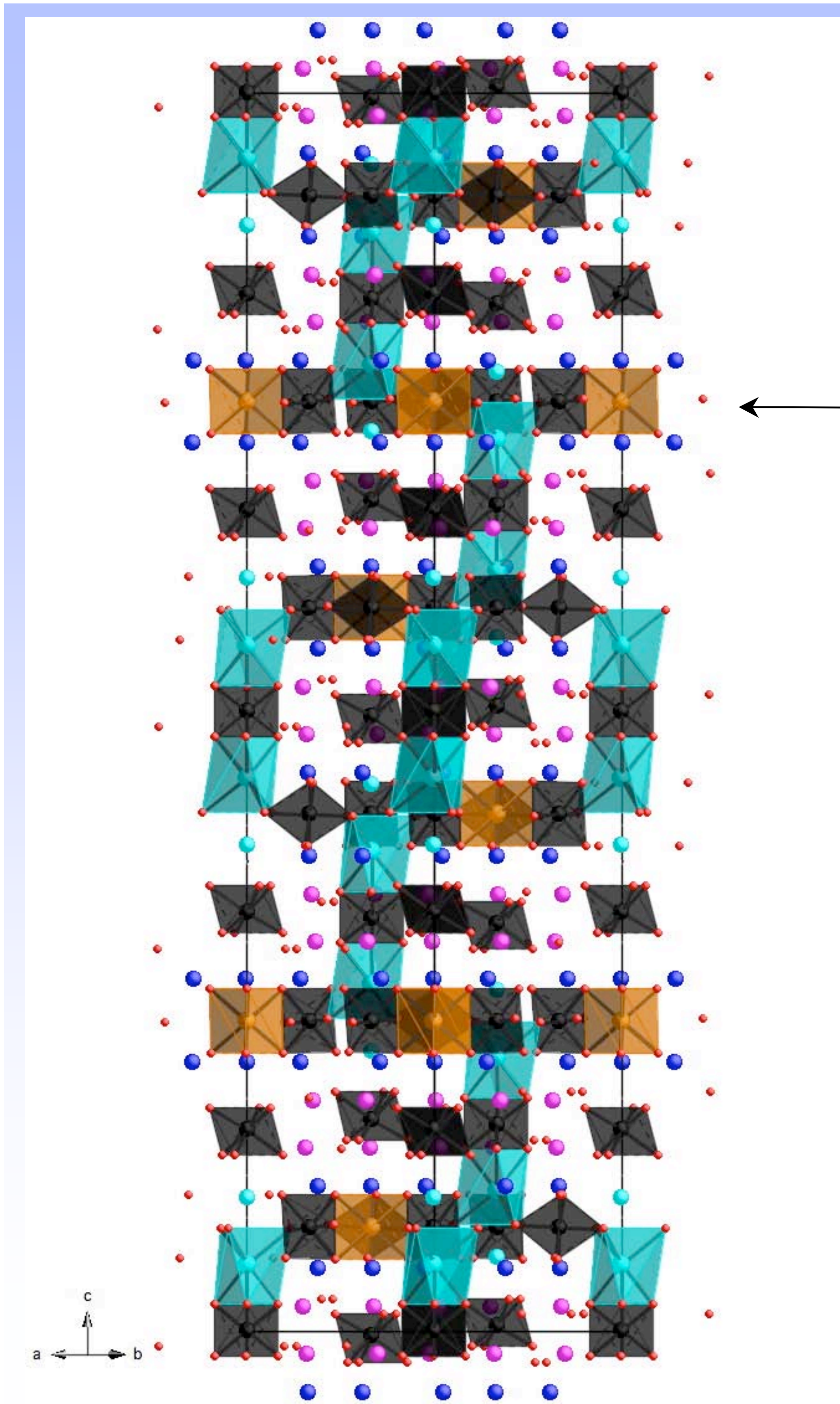
In the synthesis of $Pr_{14}Na_3Ru_6O_{36}$ osmium was present in the flux. Some small amount may have been incorporated into the crystal.

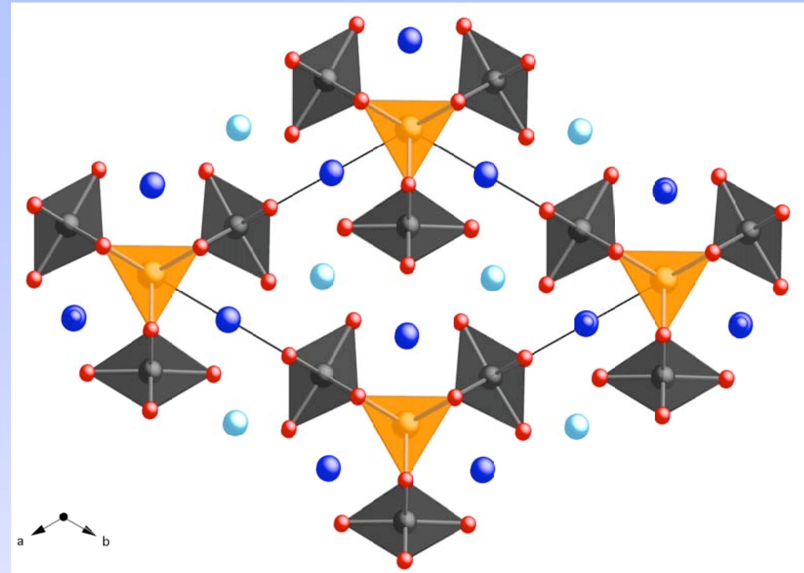


Structure of $Ln_{14}Na_3Ru_6O_{36}$ with a c-parameter of ~55 Å

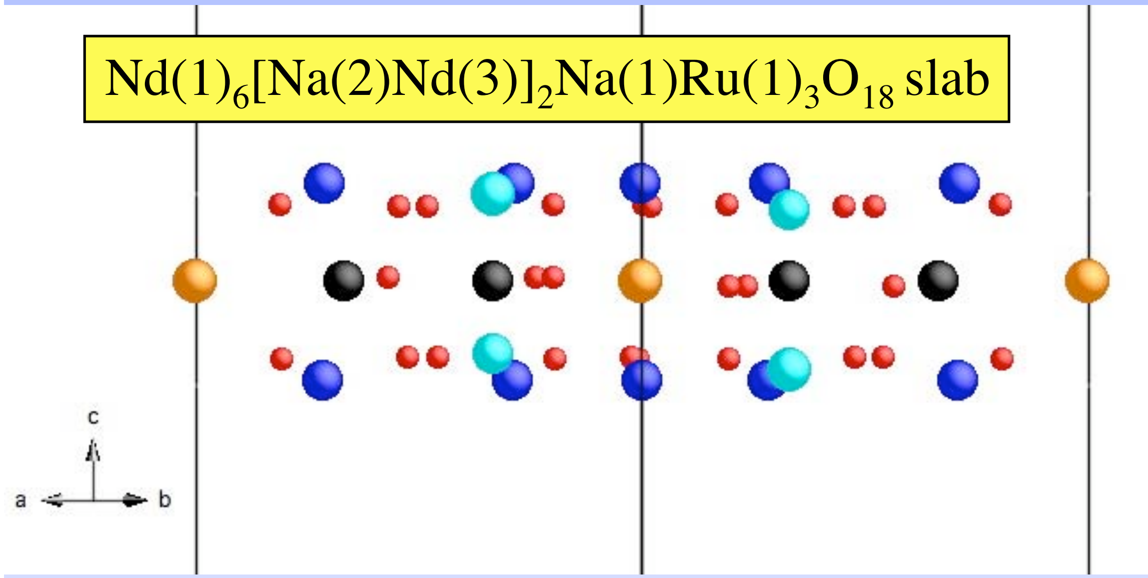
$Ru^{+4.5}$ = black
Na(1) = orange
Ln(3) = dark blue
Ln(3)/Na(2) = light blue
O = red

Ru(1)-O	1.97-1.98	Avg:	1.977
Ru(2)-O	1.99	Avg:	1.996
Ru(3)-O	1.92-2.03	Avg:	1.980





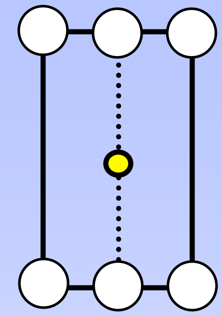
Essentially the same layer as in $LnNaIrO_4$



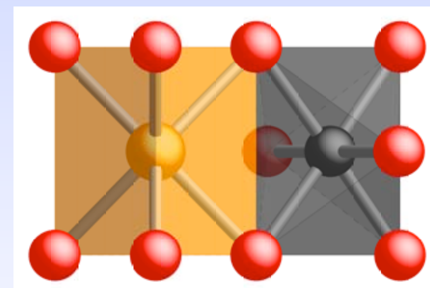
$Nd_3(Na_{0.5}Nd_{0.5})_2O_6$

$NaRu_3O_6$

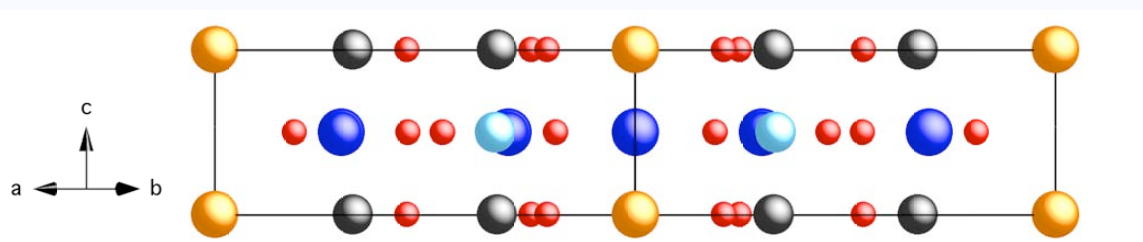
$Nd_3(Na_{0.5}Nd_{0.5})_2O_6$



Na(1): orange
Ru(1): black
Na(2)/Nd(3): light blue
Nd(3): dark blue



$LnNaIrO_4$

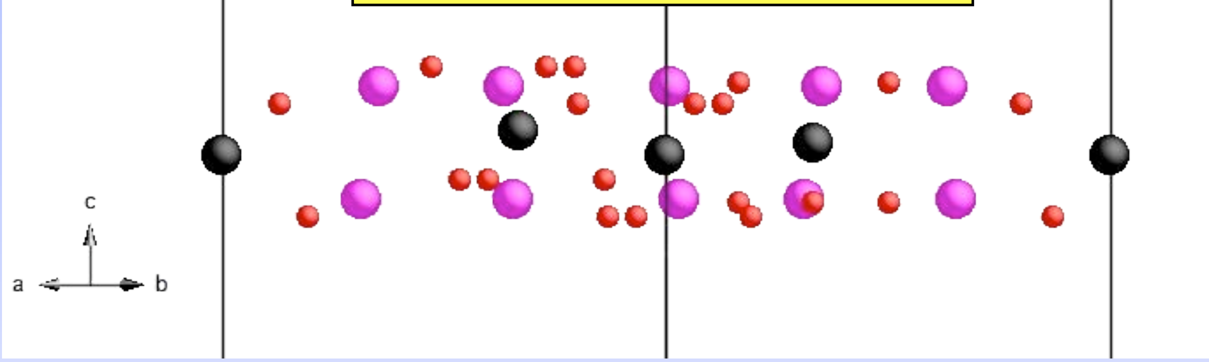


$NaIr_3O_6$

$(Ln_{1/3}Na_{2/3})_6Ln_4O_{12}$

$NaIr_3O_6$

$Nd(2)_6Ru(2)Ru(3)_2O_{18}$ slab



$Nd(2)_3O_9$

$Ru(2)Ru(3)_2$

$Nd(2)_3O_9$

Nd(2): magenta

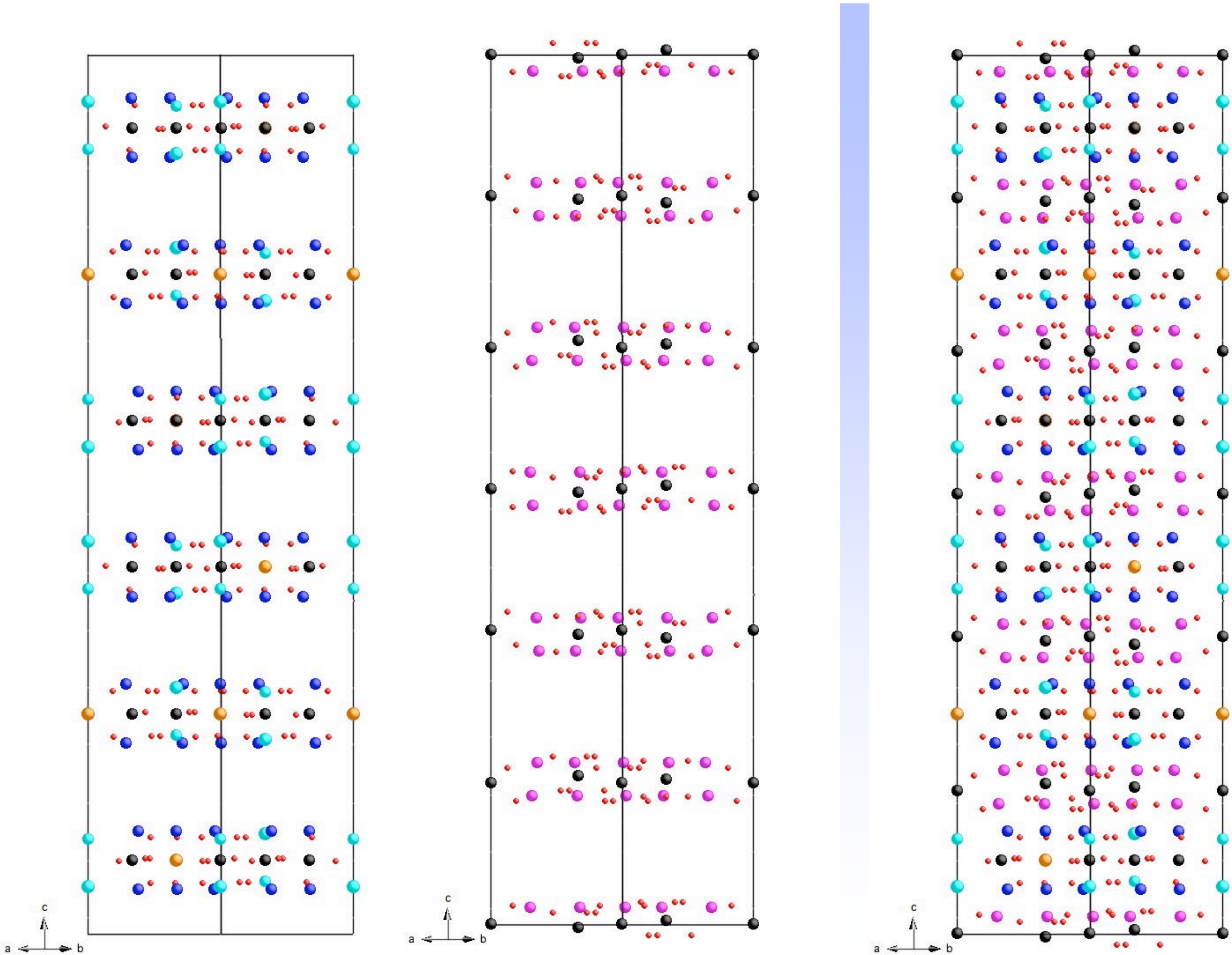
Ru(2)/Ru(3): black

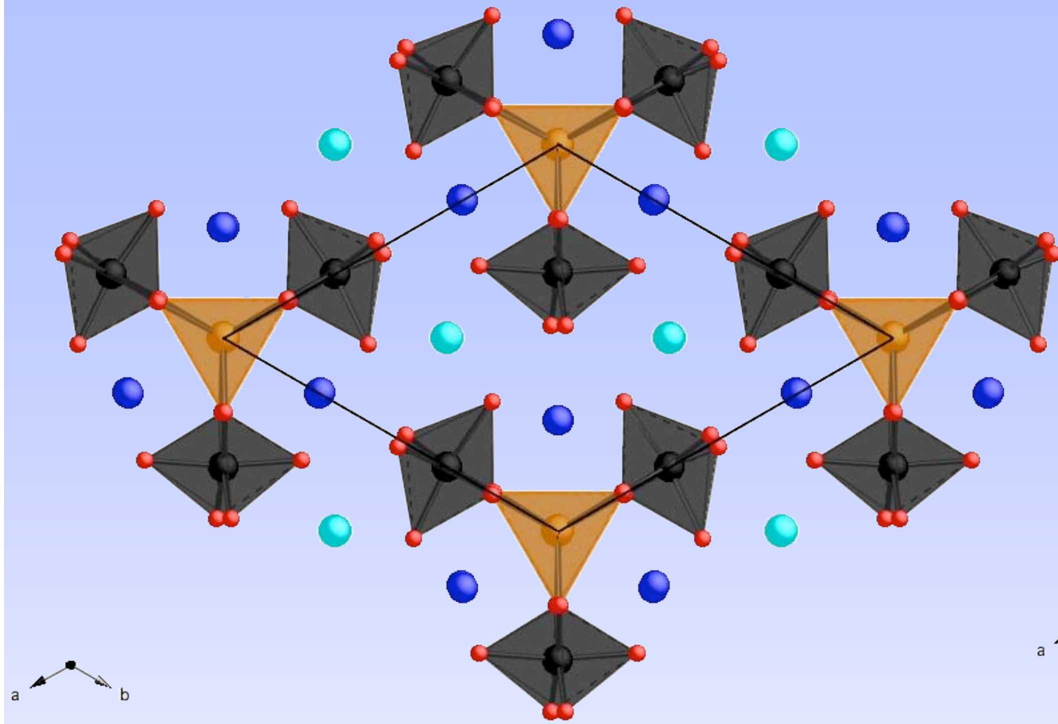
$Nd(1)_6[Na(2)Nd(3)]_2Na(1)Ru(1)_3O_{18}$ slab

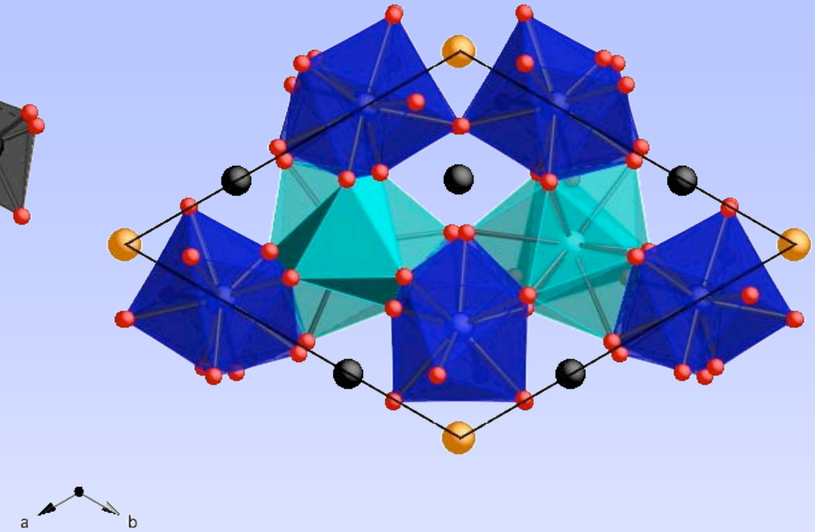
$+\ Nd(2)_6Ru(2)Ru(3)_2O_{18}$ slab

$Nd(1)_6Nd(2)_6[Na(2)Nd(3)]_2Na(1)Ru(1)_3Ru(2)Ru(3)_2O_{36}$

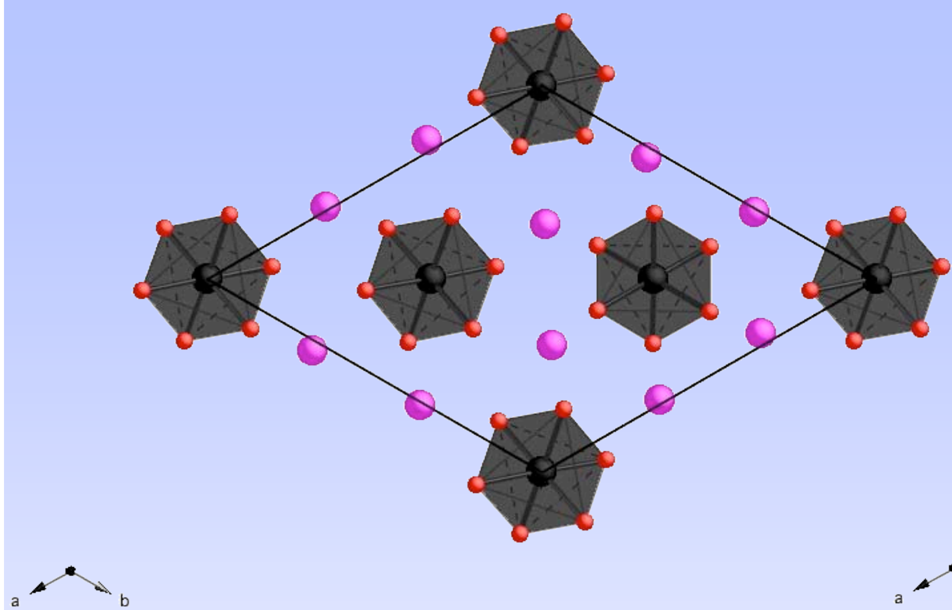
Which condenses to $Nd_{14}Na_3Ru_6O_{36}$!

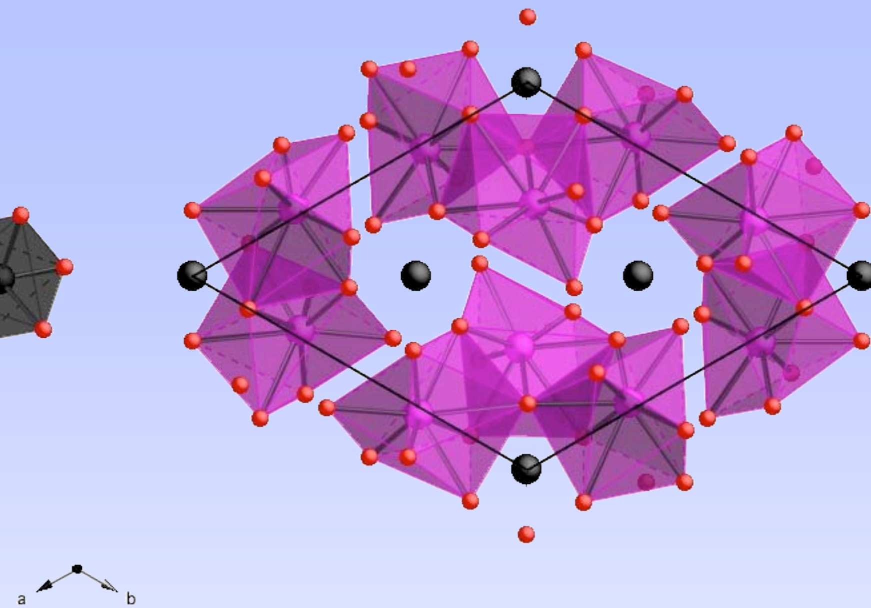

c
a
b
c
a
b
c
a
b



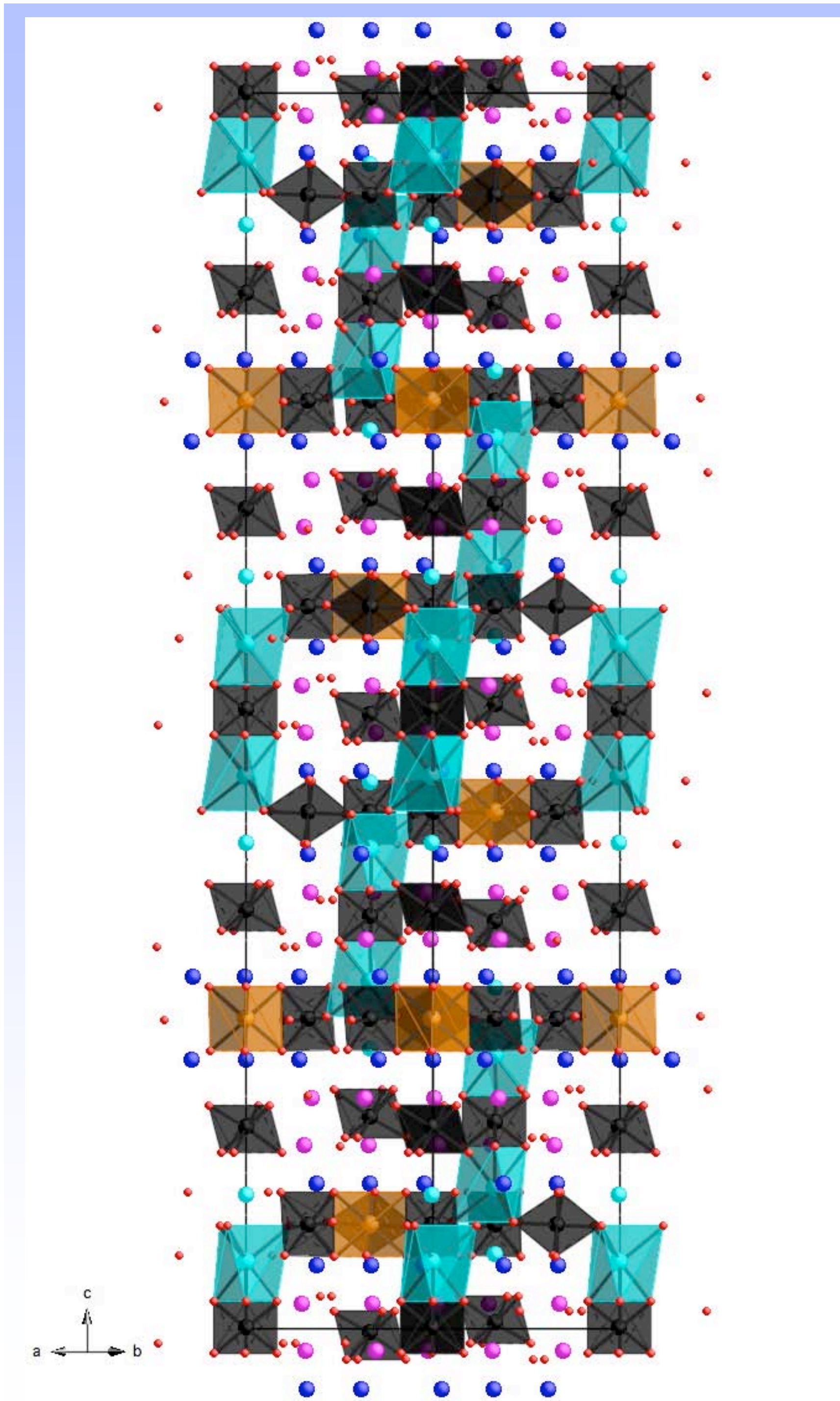


$Na(1)O_6$ trigonal prisms: orange
$Ru(1)O_6$ octahedra: black
$Nd(1)O_8$ bicapped trigonal prisms: dark blue
$Nd(3)O_9$ tricapped trigonal prisms and $Na(2)O_6$ trigonal prisms: light blue

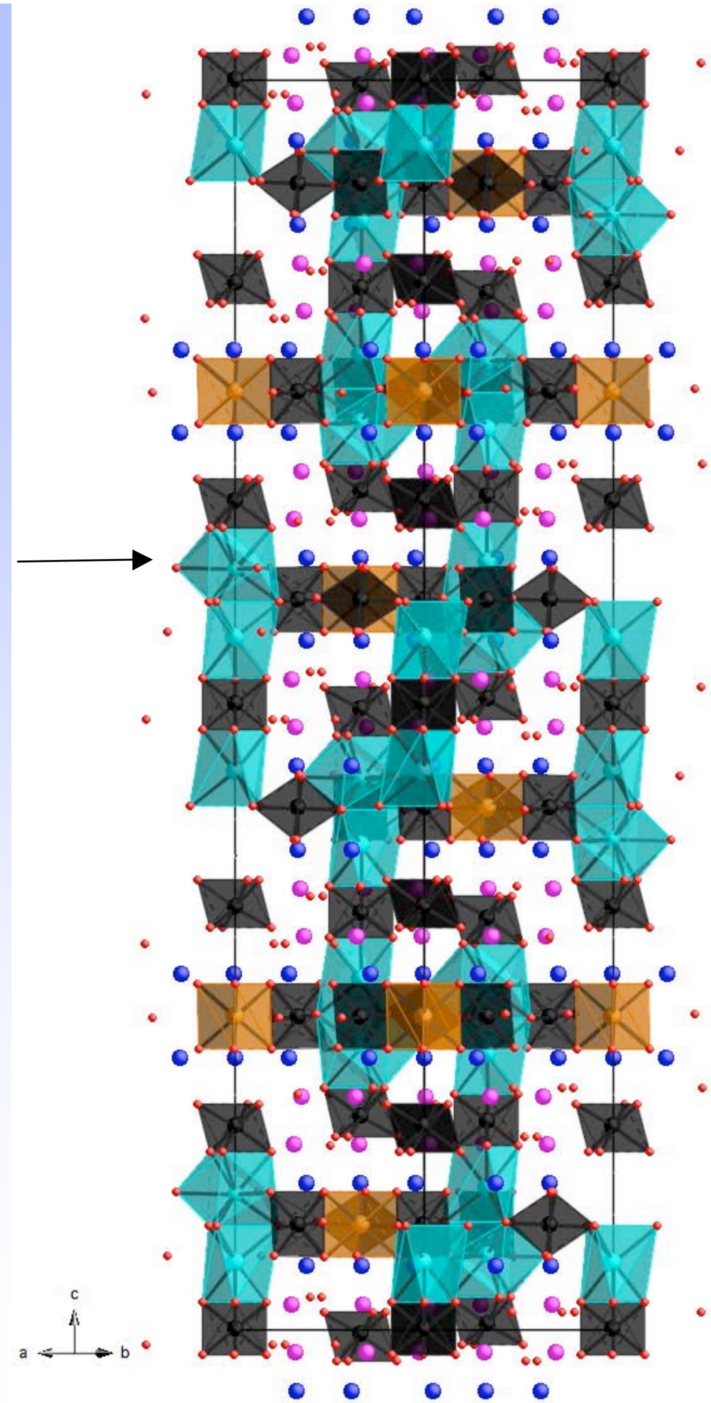




$Ru(2)O_6$/$Ru(3)O_6$ octahedra: black
$Nd(2)O_8$ bicapped trigonal prisms: magenta



Nd(3)



Conclusions

✶High temperature solutions are an excellent medium for growing oxide single crystals, as exemplified by the single crystal growth of new ruthenium, iridium and rhodium containing oxides.

✶In particular, hydroxide melts open up a higher oxidation state regime which is typically hard to reach by traditional solid state routes.

✶The use of alkali metal cations leads to some rather interesting oxidation state requirements.

✶Sodium in these oxide structures can end up in trigonal prismatic environments as well as result in mixed occupancy with rare earths.

Acknowledgements

- Financial support for this research was provided by the Department of Energy through Grant DE-FG02-04ER46122 and the National Science Foundation through Grant DMR:0450103.
-

Will Gemmill

Dr. Matt Davis

Sam Mugavero

Dr. Rene' Macquart

Dr. Mark Smith