Solid state metathesis reactions as a conceptual tool in the synthesis of new materials

presented by

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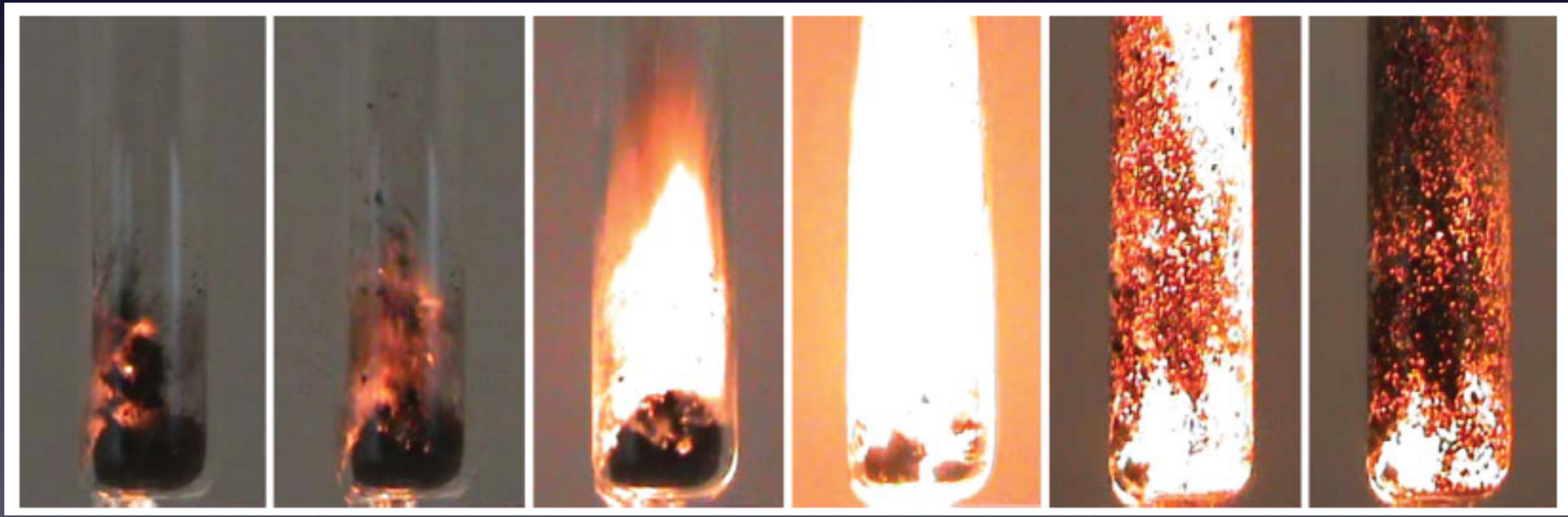
Introduction

- Solid state reactions usually involve thermodynamically controlled reactions
- Sufficiently high temperatures are necessary
- High temperature reactions lead to a strong limitation of thermal labile compounds
- Solid state metathesis (SSM) reaction takes advantage of the intrinsically energy

Introduction

- SSM reactions are initiated by ignition temperature (T_i)
- After ignition: $T_{intrinsic} \rightarrow$ 1000°C or higher

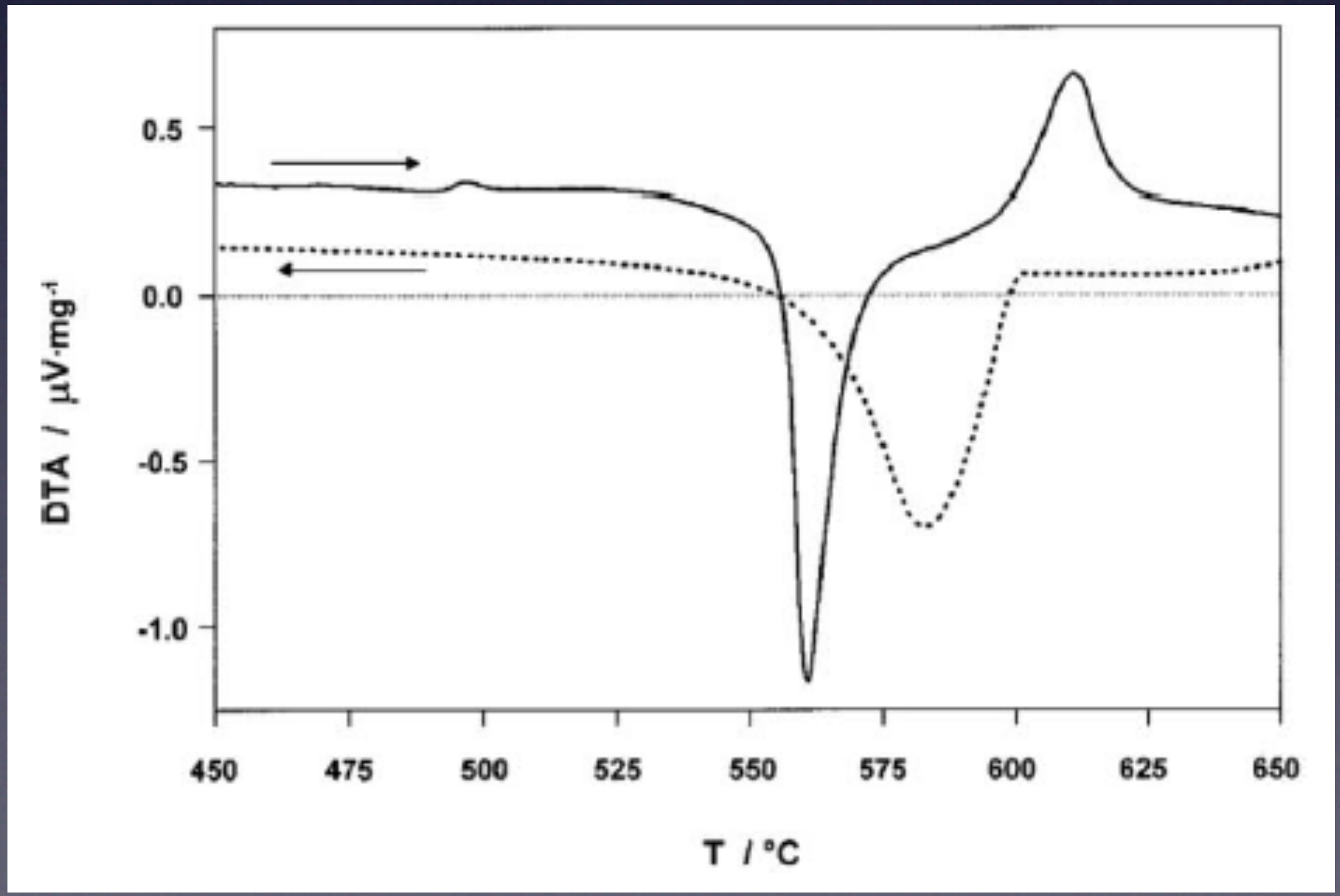


$NbCl_5$ + Li_3N reaction proceed within 0.2 seconds !

Syntheses of RE nitridoborates

- Rare earth nitridoborates:
  Preparation needs reaction temperature higher 1400°C

$$3\ RECl_3 + 3\ Li_3(BN_2) \rightarrow RE_3(B_3N_6) + 9\ LiCl$$



Syntheses of RE nitridoborates

- SSM reactions in the field of rare earth nitridoborates include syntheses of insulating, metallic, and superconducting compounds
- SSM reactions can be employed for syntheses of other systems like rare earth carbodiimides

Syntheses of RE carbodiimides

- SSM reaction of REX_3 + $Li_2(CN_2)$ (X=Cl, F)

1. High purity starting materials are loaded in silica tubes under argon (glove box)
2. Mixture is heated slowly up to ignition temperature (450 - 550°C) , reaction takes place
3. Temperature is remained for a few days before mixture is cooled down to room temperature

A flux (LiCl/KCl mixture) can be used to lower the reaction temperature!

Syntheses of RE carbodiimides

- Stoichiometry of starting materials predefines the composition of the product:

$$2\,REX_3 + 3\,Li_2(CN_2) \rightarrow RE_2(CN_2)_3 + 6\,LiX$$

$$REX_3 + 2\,Li_2(CN_2) \rightarrow LiRE(CN_2)_2 + 3\,LiX$$

$$REX_3 + Li_2(CN_2) \rightarrow REX(CN_2) + 2\,LiX$$

$$2\,REX_3 + 2\,Li_2(CN_2) \rightarrow LiRE_2X_3(CN_2)_2 + 3\,LiX$$

Compounds and structures

$RE_2(CN_2)_3$ - Rare earth carbodiimide

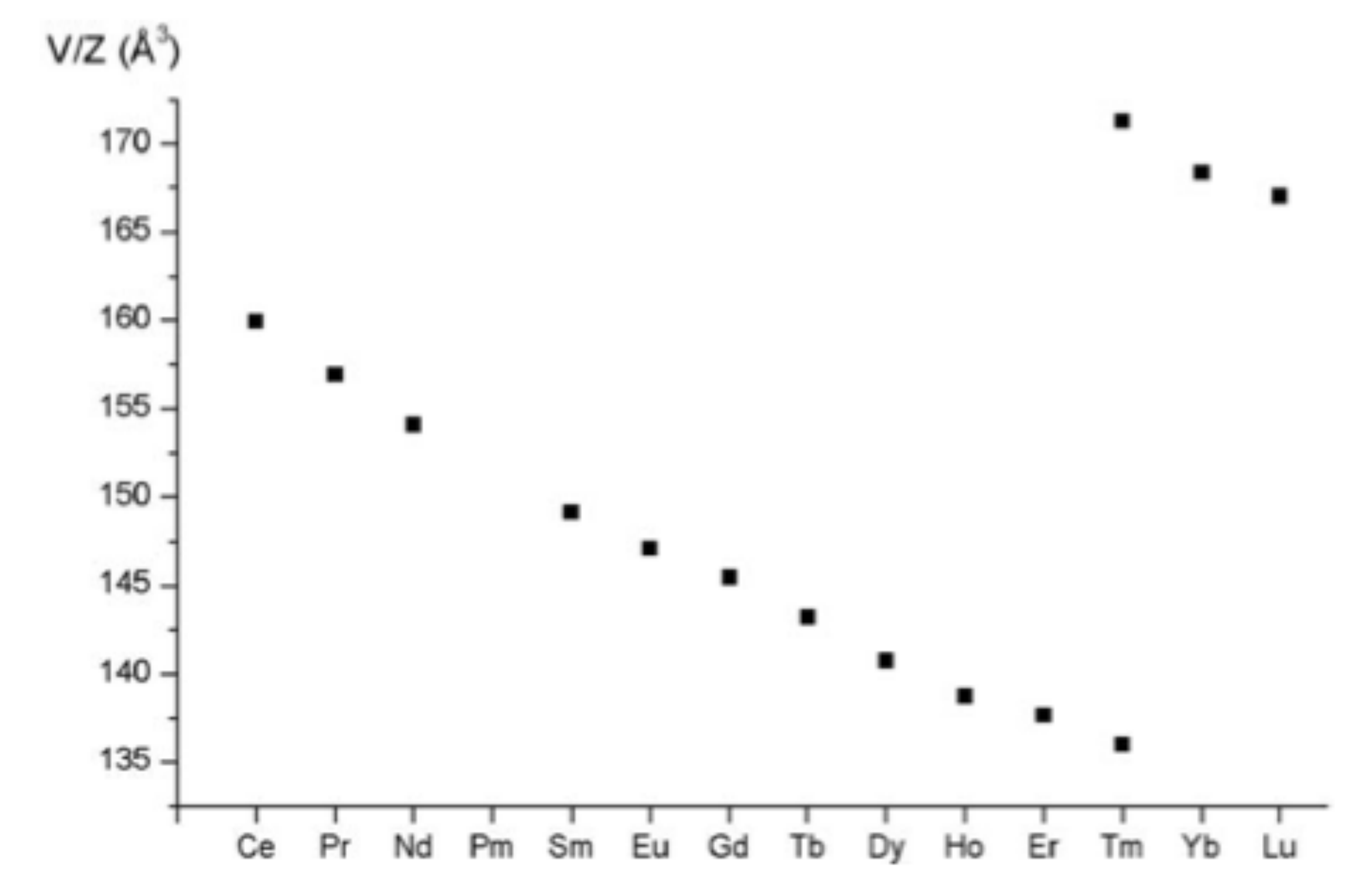


Fig. 4 Volumes (V/Z) of $RE_2(CN_2)_3$ compounds forming monoclinic structures for RE = Ce–Tm, and rhombohedral structures for RE = Tm–Lu.

Ion	Radii CN=6
Ce^{3+}	101 pm
Pr^{3+}	99 pm
Nd^{3+}	98 pm
Sm^{3+}	96 pm
Eu^{3+}	95 pm
Gd^{3+}	94 pm
Tb^{3+}	92 pm
Dy^{3+}	91 pm
Ho^{3+}	90 pm
Er^{3+}	89 pm
Tm^{3+}	88 pm
Yb^{3+}	87 pm
Lu^{3+}	86 pm

Compounds and structures

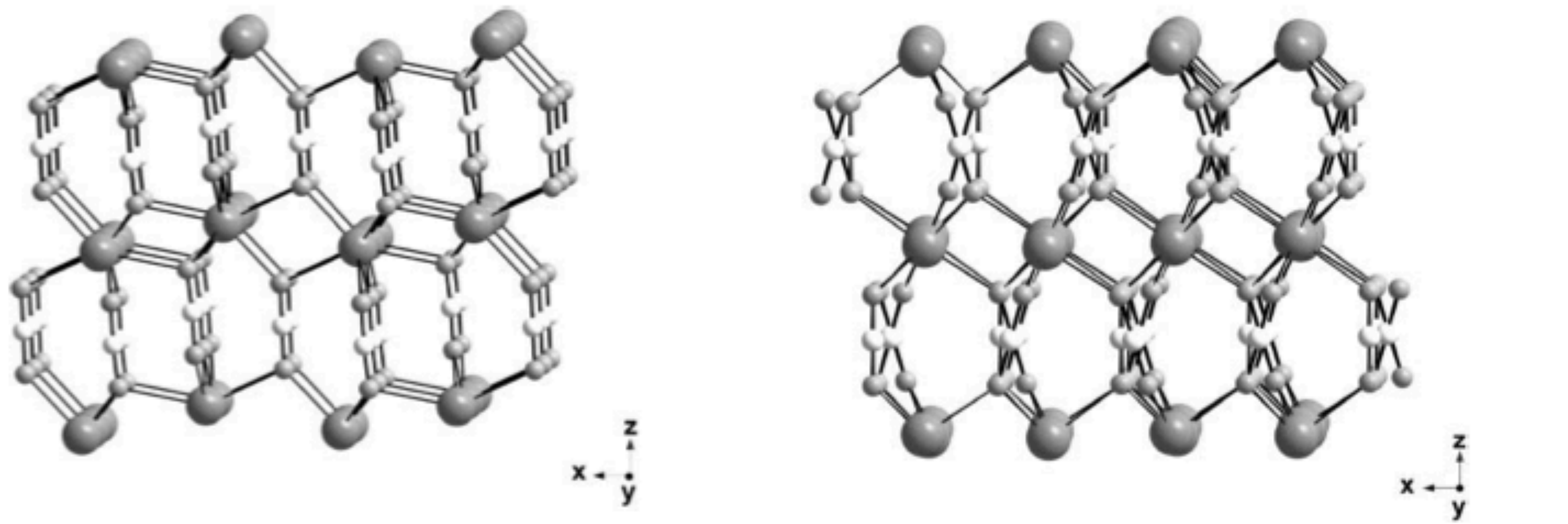


Fig. 5 Sections from layered structures of monoclinic $RE_2(CN_2)_3$-I (left) and rhombohedral $RE_2(CN_2)_3$-II (right).

Monoclinic $Tm_2(CN_2)_3$-I → Rhombohedral $Tm_2(CN_2)_3$-II

Volume increase of 20%

Luminescence properties

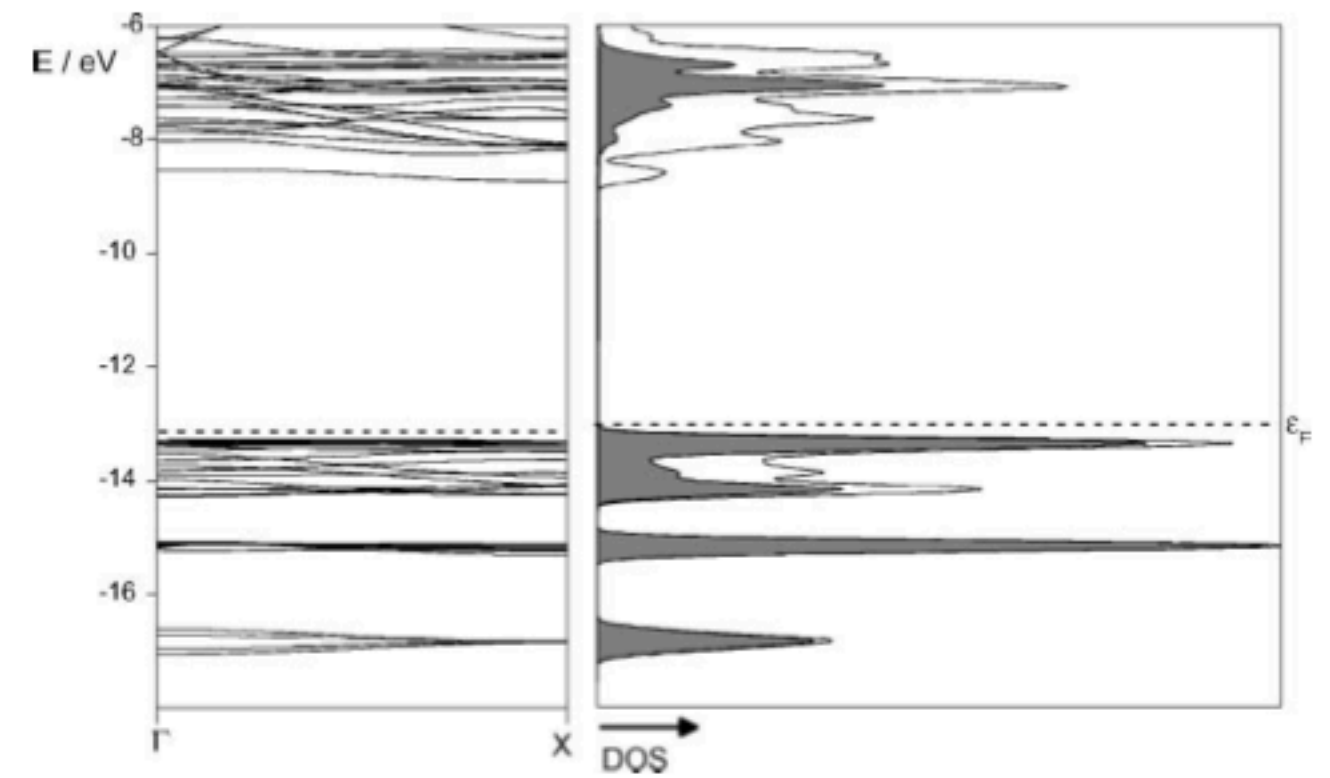


Fig. 8 A section of the band structure (along the chain direction) and the DOS of $La_2Cl(CN_2)N$. Orbital contributions of the $[NCN]^{2-}$ ion to the total DOS are projected in gray. The fermi energy (ε_f) is shown as a dashed line.

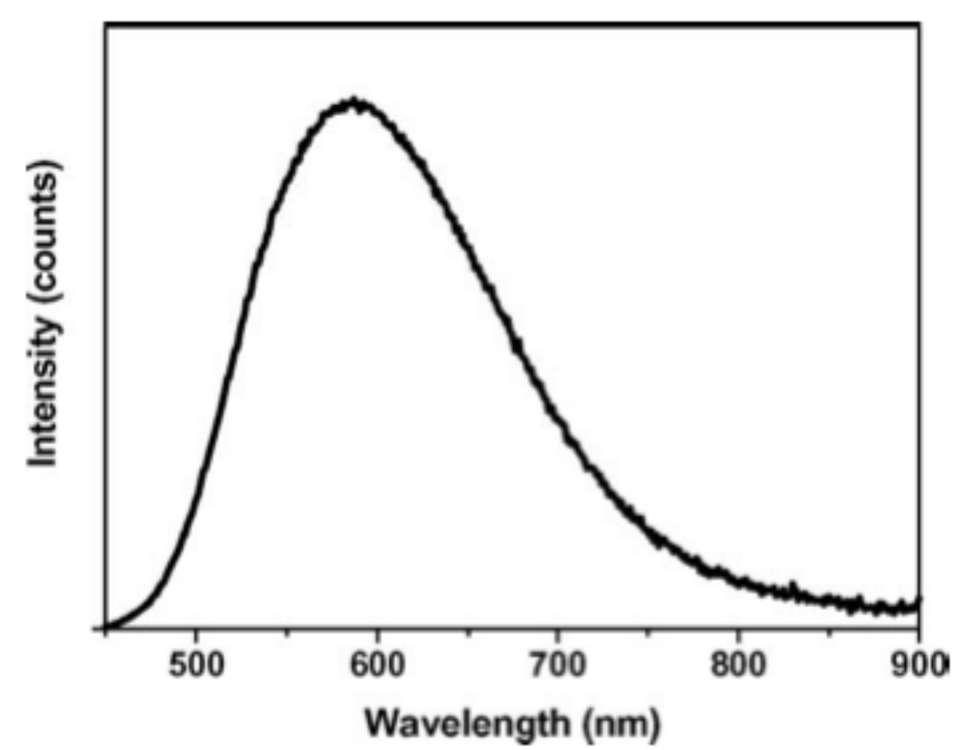


Fig. 9 Emission spectrum of $Gd_2(CN_2)_3$:Ce on excitation at 415 nm.

$Gd_2(CN_2)_3$:Ce slightly red shifted (by 15 nm) compared to $Y_3Al_5O_{12}$:Ce

Miscellaneous examples

- Transition metal carbodiimides $M(CN_2)$ with M=Mn,Fe,Co,Ni,Cu
- Tetracyanoborates and tetracyanamidosilicates e.g. $Li[B(CN)_4]$ and $KTb[Si(CN_2)_4]$
- Non metallic carbon nitrides like C_3N_4
- Dicarbides e.g. LaC_2

- And many more ways to employ SSM reactions...

Conclusion

- SSM reaction is a synthesis tool for new anions, mixed anions and complex anions
- Due to the limited thermal stability of these exotic compounds no solid state reaction applicable
- Controlled by the choice of the starting materials
- A flux can be used to lower the ignition temperature
- Method still require thermodynamical information and further calculations