Characteristics of Hf(*M*)SiBCN (*M* = Y, Ho, Ta, Mo) materials: role of the *M* choice

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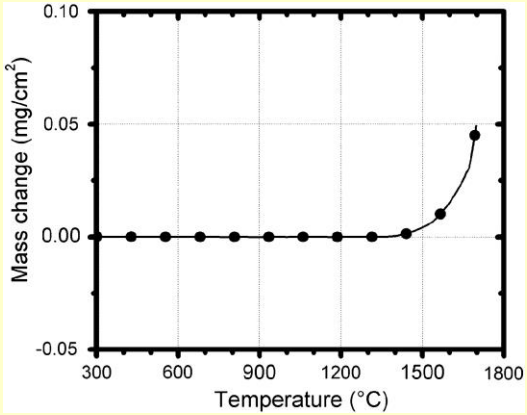
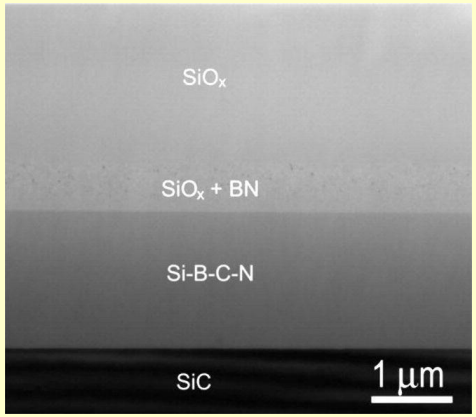
Motivation

- SiBCN thin films: high hardness (>20 GPa), thermal stability and oxidation resistance



[J. Vlcek *et al.*, *Surf. Coat. Technol.* 226 (2013) 34–39]



[J. He *et al.*, *Thin Solid Films* 542 (2013) 167–173]

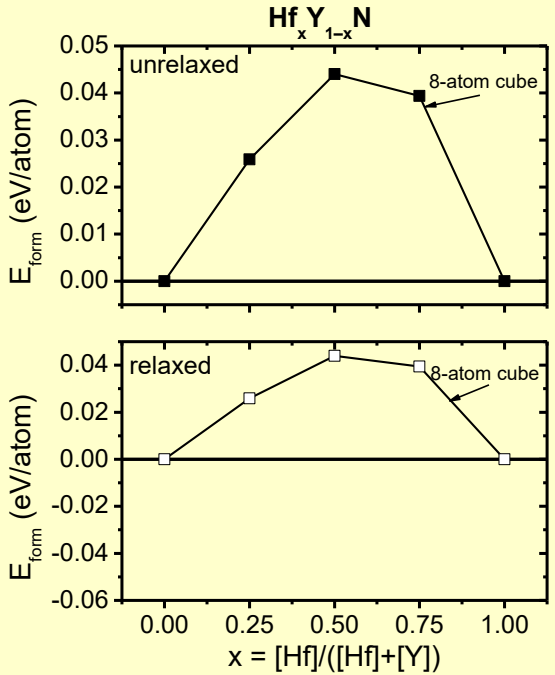
- Hf addition: enhanced electrical conductivity
- aim: explanation of properties of Hf*M*SiBCN films with a second metal element (*M* = Y, Ho, Ta, Mo or an enhanced Hf content)

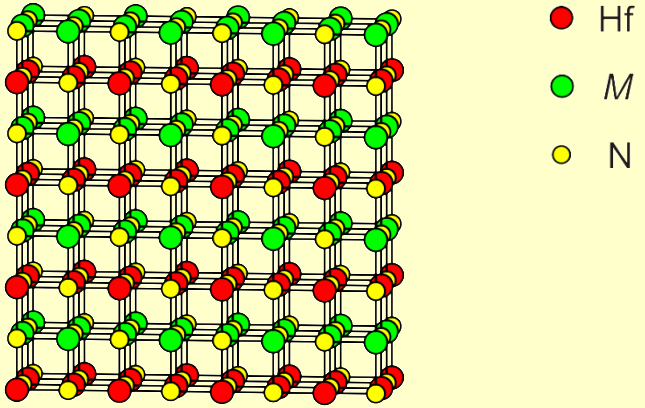
Methods

- density-functional theory calculations
  - crystalline $Hf_xM_{1-x}N$ (x = 0.00, 0.25, 0.50, 0.75, 1.00)
  - pseudopotentials + plane waves, GGA
- Car–Parrinello molecular dynamics
  - amorphous Hf*M*SiBCN
  - liquid-quench algorithm with 2 ps timescale
- pulsed magnetron sputtering
  - amorphous Hf*M*SiBCN films (1.33–1.75 µm)
  - composite target $Hf_{15-20}M_5Si_{15-30}(B_4C)_{45-65}$
  - 0.5 Pa reactive gas: 85% Ar + 15% N_2
  - pulse length 50 µs, duty cycle 50%

Formation energy of crystalline $Hf_xM_{1-x}N$

- various atomic distributions in cubic $Hf_xM_{1-x}N$ lead to various formation energies





8-atom cube:
homogeneous (100) + 2×(110) planes

Formation energy of crystalline $Hf_xM_{1-x}N$

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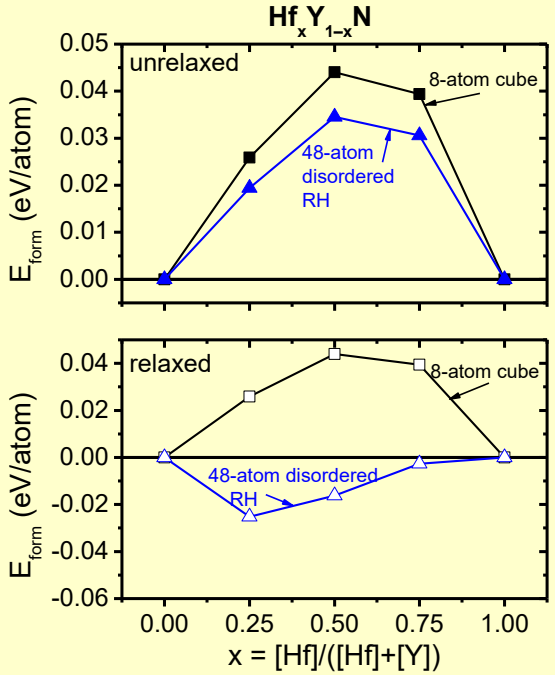

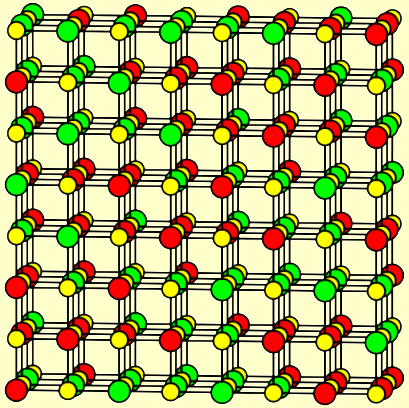

Hf
M
N

48-atom disordered rhombohedron (RH): quasirandom structure

[B. Alling *et al.*, *Phys. Rev. B* **75** (2007) 045123]

Formation energy of crystalline $Hf_xM_{1-x}N$

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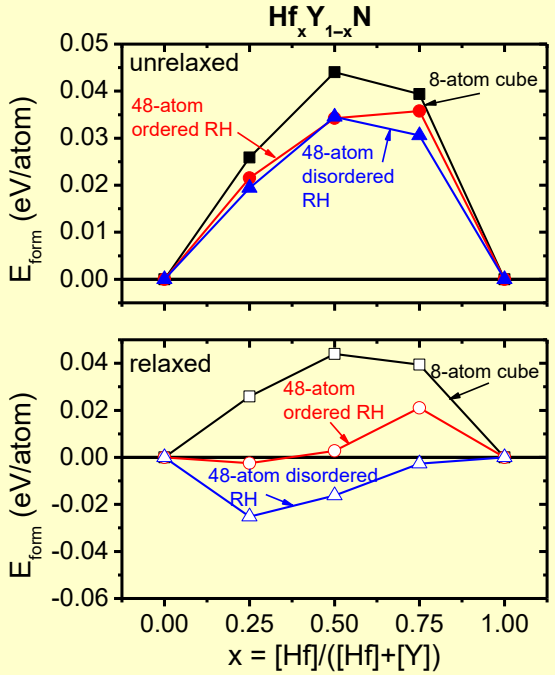

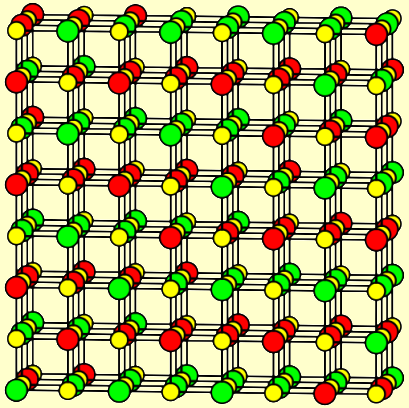

Hf

M

N

48-atom ordered rhombohedron (RH): homogeneous [110] directions

Formation energy of crystalline $Hf_xM_{1-x}N$

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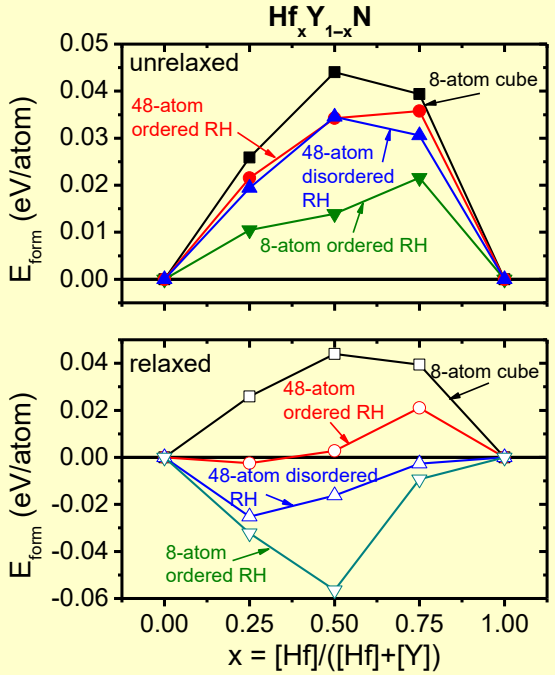
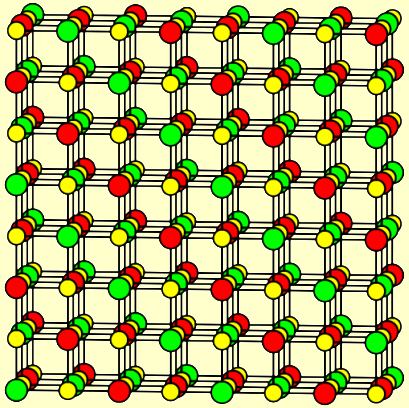




Hf

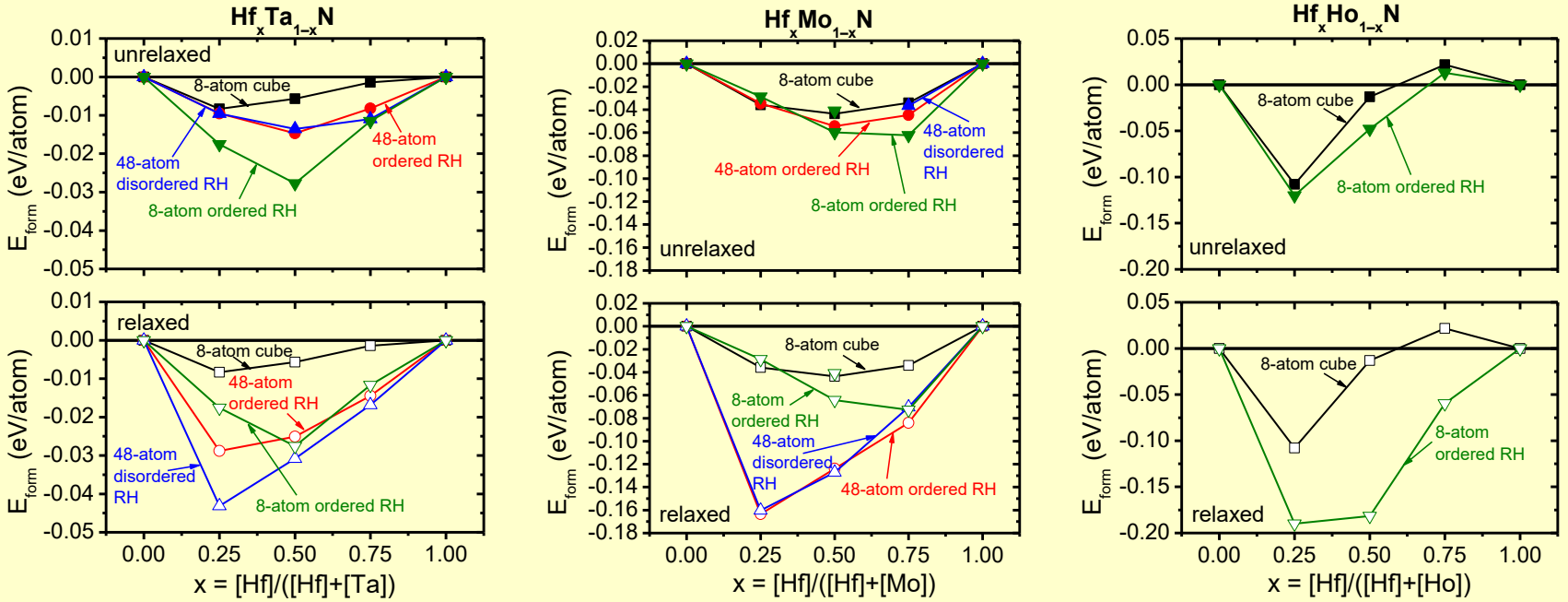
M

N

8-atom ordered rhombohedron (RH): homogeneous (111) planes

Formation energy of crystalline $Hf_xM_{1-x}N$

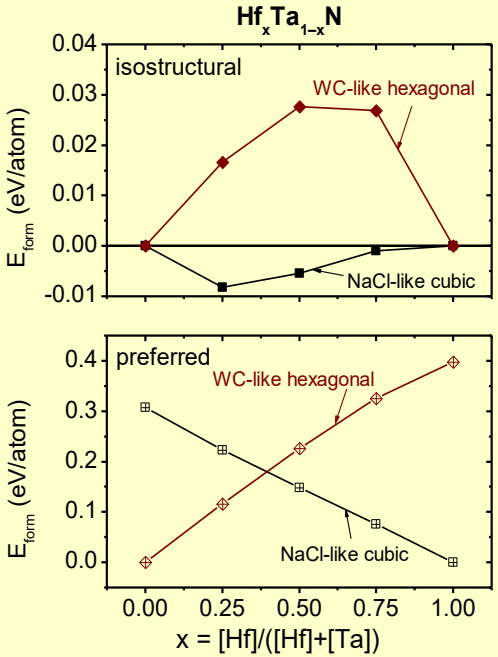
- E_{form} dependence on atomic distribution

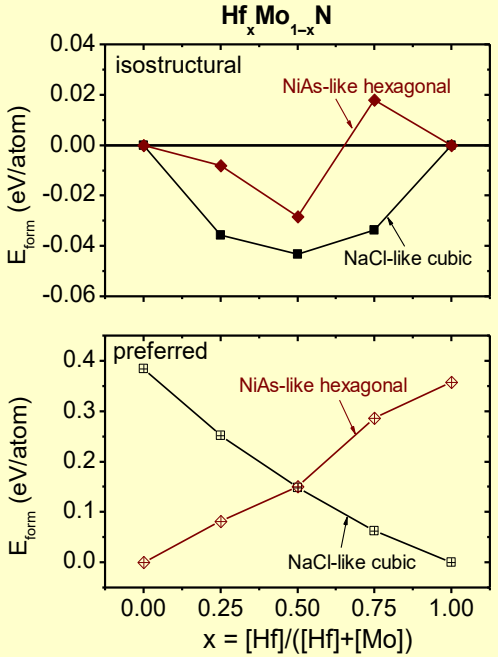


- different metals prefer different distributions of Hf and M atoms in cubic $Hf_xM_{1-x}N$

Formation energy of crystalline $Hf_xM_{1-x}N$

- E_{form} dependence on crystalline structure

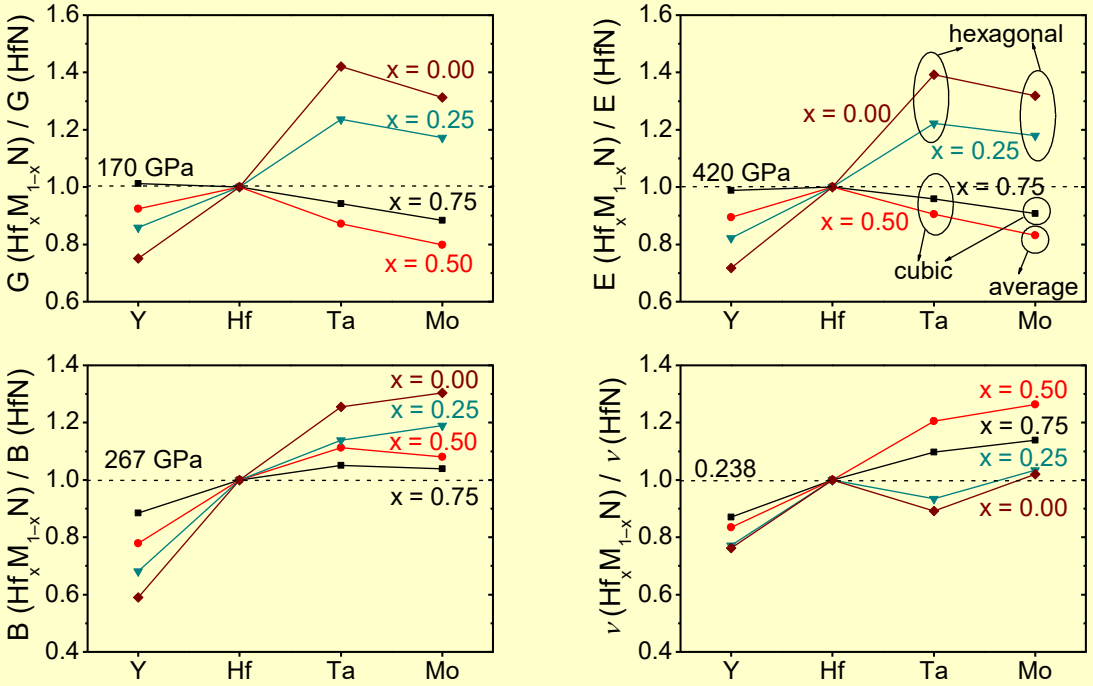




$Hf_xTa_{1-x}N$ hexagonal at $x < 0.375$, cubic at $x > 0.375$

$Hf_xMo_{1-x}N$ hexagonal at $x < 0.5$, cubic at $x > 0.5$

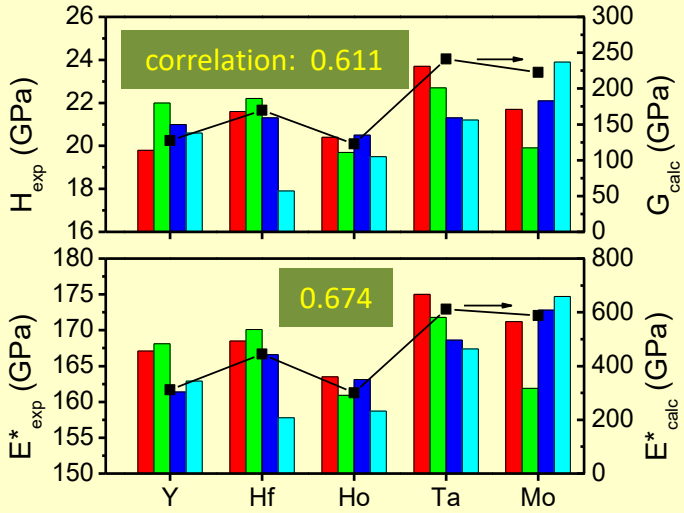
Mechanical properties of crystalline $Hf_xM_{1-x}N$



- possible enhancement of *B*, *G*, *E*, *v* of HfN by alloying with TaN or MoN
- non-monotonic dependence of *G*, *E*, *v* on *x*

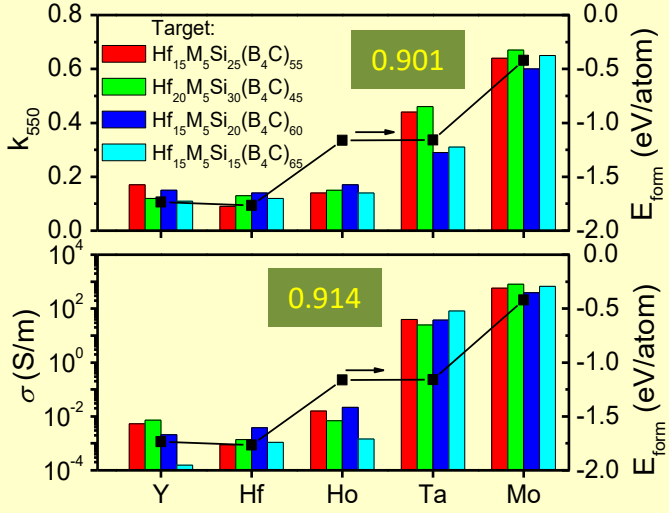
Crystalline *M*N and amorphous Hf*M*SiBCN

- mechanical properties



- reasonable correlation
- better prediction by *M*N than by $Hf_xM_{1-x}N$

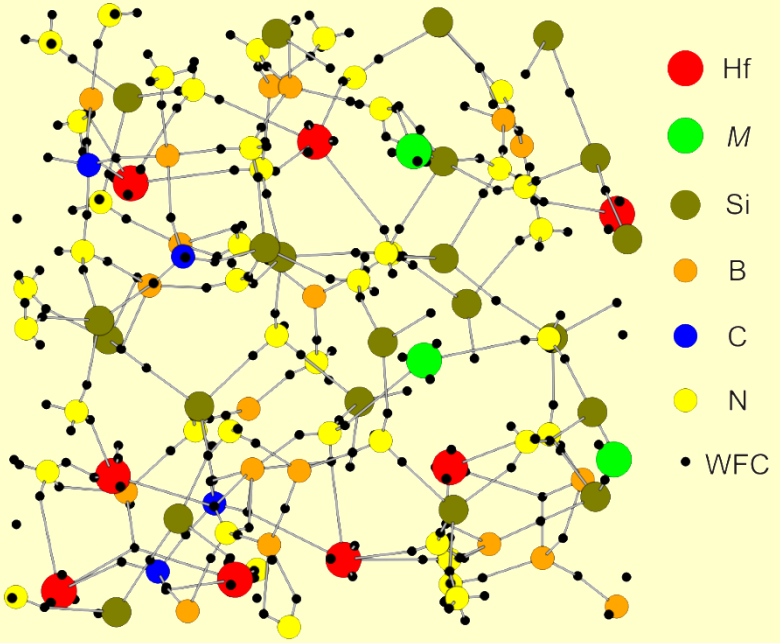
- optical and electrical properties



- high correlation
- monotonous trends with group number

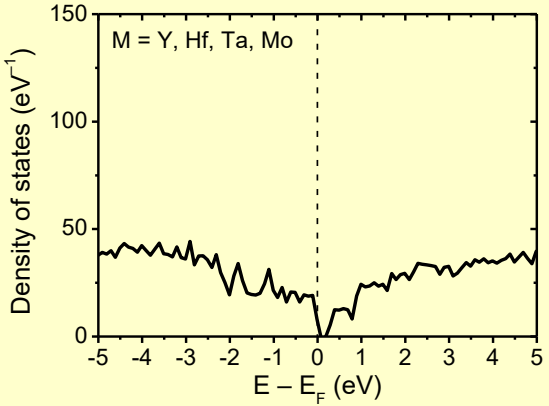
Simulated amorphous Hf*M*SiBCN

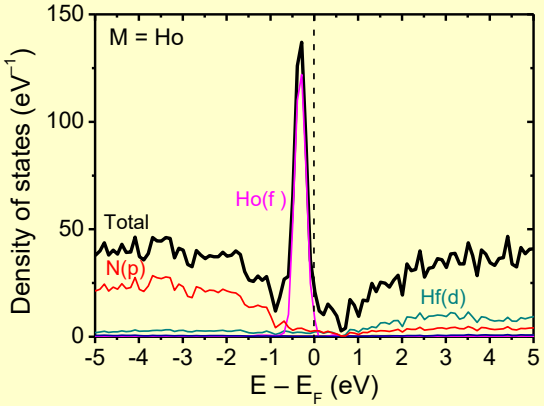
- experiment-based materials
  - $Hf_8\ Y_3\ \ Si_{22}B_{20}C_4N_{43}$
  - $Hf_{11}\ \ \ Si_{21}B_{21}C_4N_{43}$
  - $Hf_8Ho_3\ Si_{22}B_{23}C_4N_{40}$
  - $Hf_8\ Ta_3\ \ Si_{22}B_{23}C_4N_{40}$
  - $Hf_8Mo_3Si_{22}B_{25}C_5N_{37}$
- packing factor 0.47
- liquid-quench algorithm



Simulated amorphous Hf*M*SiBCN

- density of electronic states





M = Y, Hf, Ta, Mo:

– confirmation of the semiconductive character

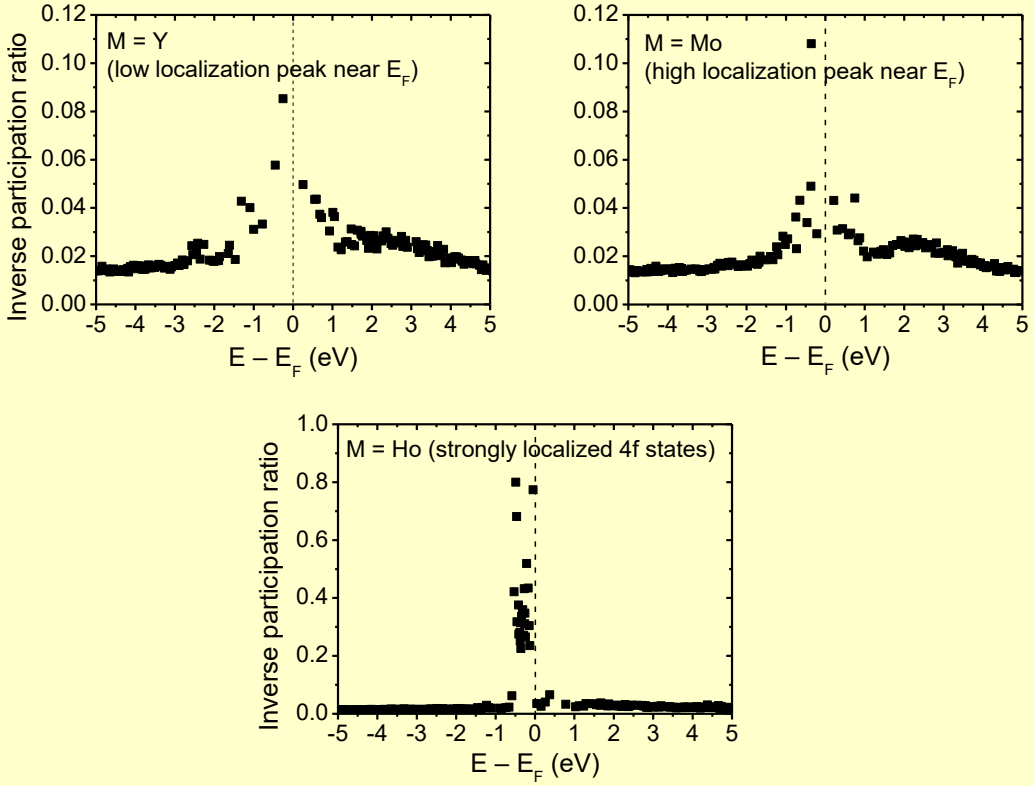
– Y → Mo:
observable narrowing of the band gap

M = Ho:

– numerous 4*f* states near the Fermi level

Simulated amorphous Hf*M*SiBCN

- localization of electronic states

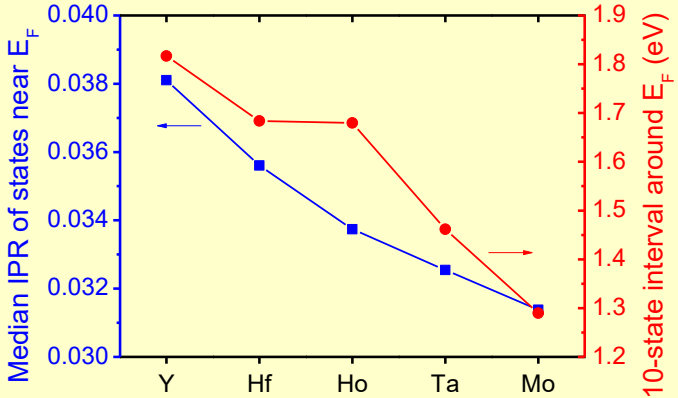


M = Y, Hf, Ta, Mo:
decent enhancement of inverse participation ratio of states near the Fermi level

M = Ho:
localized 4*f* states
at E_F do not contribute to electrical conductivity

Amorphous Hf*M*SiBCN and crystalline *M*N

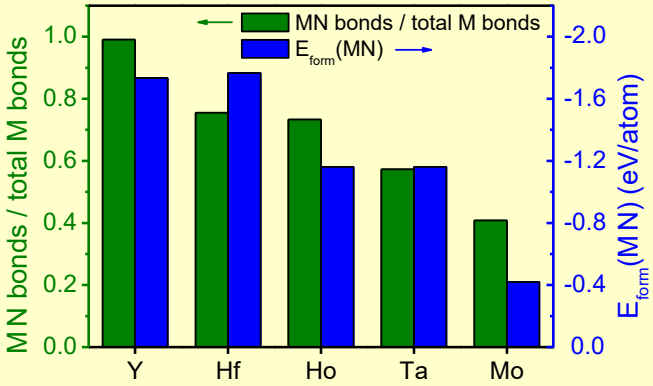
- electronic structures



Y → Mo:

- more states close to E_F
- more delocalized states

- bonding statistics

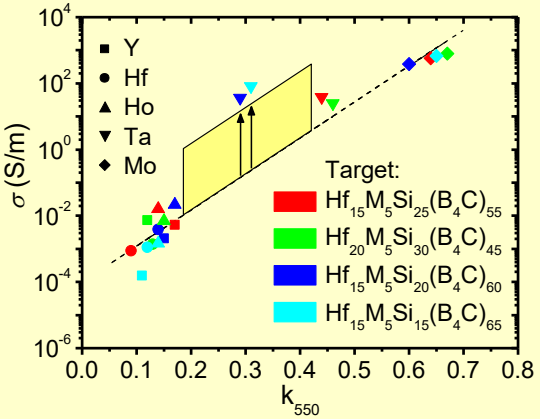


Y → Mo:

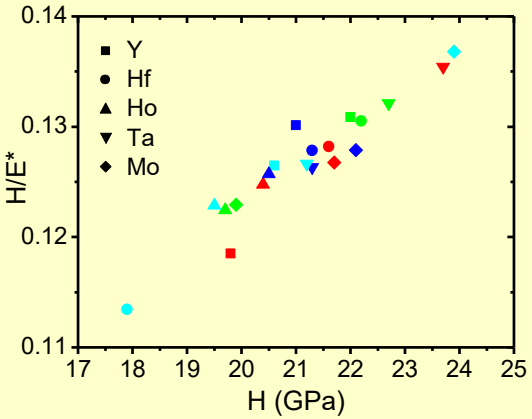
- lower preference of *M* to bind with N
- lower driving force towards N incorporation

⇒ Y → Mo: increasing metallicity of Hf*M*SiBCN

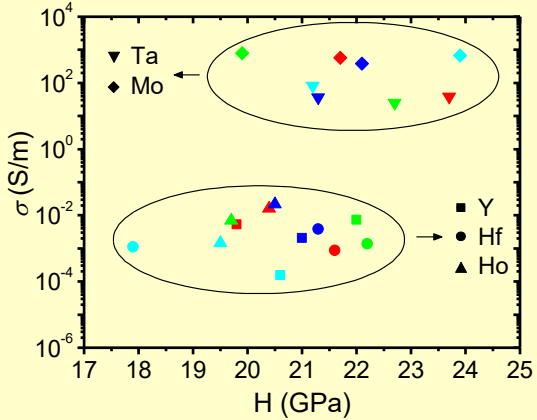
Synthesized amorphous Hf*M*SiBCN



correlation: 0.921



0.939



0.372

- correlation of conductivity and opaqueness
  - exceptionally good combinations of σ and k_{550} for targets 15% Hf, 5% Ta, 15–20% Si, 60–65% B_4C
- H/E^* strongly correlated with H
- $H > 20$ GPa achievable at any σ

Conclusions

- different metals prefer different atomic distribution in nitride solid solutions
- identical trends of properties of crystalline *M*N and amorphous Hf*M*SiBCN
  - correlated mechanical properties
  - simultaneous increase in metallicity at higher *M* group numbers (*M* = Y → Hf → Ho → Ta → Mo)
- preparation of films combining high hardness and thermal stability with relatively high electrical conductivity and optical transparency using targets $Hf_{15}Ta_5Si_{15–20}(B_4C)_{60–65}$