USPEX SCHOOL 2020

Search for materials with optimal properties

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Outline

• Search for superhard materials with optimal hardness based on binary transition metal borides

• Hunt for superconducting compounds among the metal hydrides at high-pressures
Hard and Superhard materials

- **Diamond**: 98 GPa
- **c-BN**: 60 GPa
- **WC**: 30 GPa
- **TiN**: 25 GPa
- **TiB₂**: 50 GPa
- **CrB₄**: 50 GPa

Superhard Materials

Ease in synthesis and production
High melting temperature
High hardness

The main direction of developments in this field of technology is replacement of traditional materials by new ones with improved properties.

PCD, c-BN, Mixture PCD/BN
Hard alloys of WC, TiN etc.

Substitution of traditional materials
W-B System. “WB₄” Structure

There are many experimental studies devoted to synthesis of superhard compound with preliminary composition of “WB₄”, but theoretical studies reported about the composition between WB₃ and WB₁₂.

Controversial data about the crystal structure of higher tungsten boride leads to ambiguous conclusions about its properties.

W-B System. $\text{WB}_5$ Structure
W-B System. \( \text{WB}_5 \) Structure

New higher boride \( \text{WB}_5 \) was predicted, which has unique mechanical properties and potentially can be used instead of traditional hard alloys.

Vickers hardness is 45 GPa

Temperature stability

Wide temperature range of stability of WB$_5$ makes it a perspective material for big number of potential applications in industry

Mechanical properties

New compound with unique combination of hardness and fracture toughness was predicted

Synthesis and properties of higher tungsten boride

Using high-temperature sintering of boron and tungsten nanometer-size powders the highest tungsten boride was synthesized.

Measurements of Vickers microhardness of synthesized $\text{WB}_{5-x}$ samples show that they 30-50% harder (depending on synthesis conditions) than $\text{94WC-6Co}$, which confirms our predictions.

Synthesized compound has higher symmetry compared to predicted one ($P6_3/mmc$) and does not have WB$_5$ composition. Non-stoichiometric disordered structures need to be considered.
Refinement of structure

Synthesized compound is $\text{WB}_{5-x}$
Models for structure refinement were proposed

Crystal structure is disordered and composition varies from $\text{WB}_{4.18}$ to $\text{WB}_{4.86}$

$R_F = 0.039$

$\lambda = 1.5406 \text{ Å}$

Synthesized higher tungsten boride has structural motifs that belong to predicted WB$_5$, but has disordered structure with the composition of WB$_{4.2}$. 
1. Total energy of the supercell made of $N P6_3/mmc$-WB$_3$ unit cells can be calculated as:

$$E_{N,n} = N E_{WB_3} + n \Delta E_{B_3} + \frac{1}{2} \sum_{i \neq j} K_{ij} S_i S_j$$

2. Fit of the parameters of interaction $K_{ij}$:

<table>
<thead>
<tr>
<th>Neighbor order</th>
<th>Number of neighbors</th>
<th>Distance</th>
<th>$K$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>$c/2$</td>
<td>1.378</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>$a$</td>
<td>0.094</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>$\sqrt{a^2 + c^2/4}$</td>
<td>0.023</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>$c$</td>
<td>0.084</td>
</tr>
</tbody>
</table>

3. Search for the most stable composition, corresponding to the optimal arrangement of the B$_3$ units within WB$_3$-WB$_3$ range.
Developed lattice model proves the possibility of formation of disordered \( \text{WB}_{5-x} \) compounds during the synthesis.

Increase of temperature leads to stabilization of disordered $\text{WB}_{4.2}$ compound and predicted $\text{WB}_5$. We showed that at high temperatures the probability of the formation of disordered structure with $\text{WB}_{4.2}$ composition is highest, which is confirmed by our experiments.

Predicted “treasure” map of distribution of hard and superhard materials allows one to determine the most perspective materials for synthesis and industrial applications.

Superconducting materials

HTSC-2 ribbon based on the multilayered composite YBCO or BSCCO.

Tc = 90-110 K, j(crit) = 500 A/mm² at 77 K,
H(crit) = 20T at 4 K

MgB₂-wire, *in situ* formed according to «powder in the tube» experimental scheme

Tc = 20-25 K (up to 39 K), j(crit) = 200 A/mm² at 4K, H(crit) = 10T at 4 K
Superconducting materials

Search for stable thorium hydrides

New higher hydride – ThH$_{10}$ was predicted having the lowest stability pressure among other higher metal hydrides with very high $T_C \sim 220$ K

A.G. Kvashnin et al. ACS App. Mat. Interfaces, 10, 43809 (2018)
Synthesis of ThH$_{10}$

Results of computational search allowed us to perform targeted synthesis of high-$T_C$ ThH$_{10}$

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)
Equations of states

All predicted thorium hydrides were synthesized

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)
ZPE contribution leads to stabilization of ThH$_9$
Based on experiments we show that ZPE contribution is crucial for description of the stability of higher metal hydrides under pressure.

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)
ThH$_9$ – new high-$T_C$ superconductor

$\lambda = 2.15, \ T_C = 138 \text{ K (100 GPa)}$

$\lambda = 1.73, \ T_C = 145 \text{ K (150 GPa)}$
Experiments on ThH$_9$ and ThH$_{10}$

Performed experiments confirmed the superconducting properties of new ThH$_{10}$ and ThH$_9$.

ThH$_{10}$: $T_C = 159$ K at 174 GPa
ThH$_9$: $T_C = 146$ K at 170 GPa

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)
**Synthesis + $T_C$**

**Theory $T_C$**

**Synthesis**

H$_3$S (203 K @ 150 GPa)  
*Nature* 525, 73 (2014)

H$_3$P (100 K @ 200 GPa)  
*arXiv:1508.06224*

YH$_{10}$ (326 K @ 250 GPa)  
*PNAS* 114, 6990 (2017)

LaH$_{10}$ (260 K @ 190 GPa)  
*PNAS* 114, 6990 (2017)

CaH$_6$ (235 K @ 150 GPa)  
*PNAS* 109, 6463 (2012)

YH$_9$ (243 K @ 201 GPa)  
*arXiv:1909.10482*

ThH$_{10}$ (159 K @ 174 GPa)  
*Mat. Today* 33, 36-44 (2020)

CeH$_9$ (117 K @ 200 GPa)  

**It is necessary to provide additional theoretical studies of SC-hydrides**

UH$_7$ (55 K @ 20 GPa)  
*Phys. Rev. B* 102, 014107 (2020)

AcH$_{16}$ (200 K @ 150 GPa)  
Magnetic hydrides NdH$_9$ and NdH$_7$

D. Zhou, D.V. Semenok, ..., A.G. Kvashnin et al., JACS, 142, 2803 (2020)
Molecular metal: pseudocubic $\text{BaH}_{12}$

What is next?

Do we need to test hydride systems one by one?

**NOT NECESSARY**

**OR** maybe we can predict $T_c$ for all possible hydrides of all elements from Periodic Table?

**YES**
Distribution of **binary** high-\(T_c\) hydrides

DFT calculations, statistical analysis and neural network show that record high-TC hydrides are located in the \(d^0\), \(d^1\) and \(d^2\) regions of elements Sc-Y-La-Ac \((d^1\)-belt\), Mg-Ca-Sr-Ba-Ra \((d^0\)-belt\), and Th \((s^2d^2)\)

D.V. Semenok, ..., A.G. Kvashnin et al., Curr. Opin. Solid State Mater. Sci. 100808 (2020)
What is next?

Search for more complex compounds

Ternary hydrides (Dmitrii Semenok, November 13, 12:30)
Acknowledgements

Skoltech
Prof. A.R. Oganov
Prof. A.A. Osiptsov
Prof. A.V. Shapeev
Dr. D.V. Rybkovskiy
Dr. E.V Podryabinkin
Dr. Z. Allahyari
Dr. C. Xie
D.V. Semenok

LPI RAS
Prof. V.M. Pudalov
Dr. A.V. Sadakov
Dr. O.A. Sobolevskiy

HPPI RAS
Prof. V.V. Brazhkin
Dr. V.P. Filonenko
Dr. I.P Zibrov

IC RAS
Dr. I.A. Troyan
Dr. A.G. Ivanova
Dr. I. Luybutin

JU
Prof. T. Cui
Prof. X. Huang
Dr. D. Duan

Dr. I.A. Kruglov (VNIIA)
Prof. V.Yu. Fominski (MEPhl)
Dr. A.Ya. Zakirov (Gazpromneft-STC)
Dr. L.S. Ismailova (Saudi Aramco)
Dr. H.A. Zakaryan (ESU, Armenia)
Dr. A. Goncharov (Carnegie Institution, USA)
Dr. S. Lobanov (GFZ Postdam, Germany)

Supported by the Russian Scientific Foundation grant
No. 19072-30043 “Computational materials design laboratory”