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ORIGINAL REPORT



Discovery of ABO_3 perovskites as thermal barrier coatings through high-throughput first principles calculations

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ABSTRACT

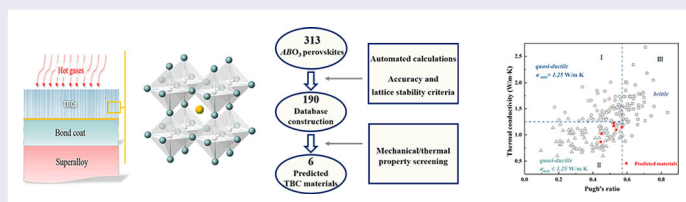
High-throughput first-principles calculations are performed on ABO_3 perovskites for new thermal barrier coating (TBC) materials. We present systematic investigations comprised of multiple selection criteria to achieve the prediction of target materials. A database including mechanical/thermal properties of 190 perovskites is initially established. Six perovskites are proposed as novel TBC materials with predicted thermal conductivities under 1.25 W/(m·K) and good damage tolerance. The observed anisotropy of thermal conductivity provides possibilities for the performance controlling via the growth orientation design. The adopted strategy and established database are expected to inspire the design of ABO_3 -based TBC materials and future structural material investigations.

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KEYWORDS

High-throughput; perovskite; thermal conductivity; first-principles calculations



IMPACT STATEMENT

An investigation strategy for ceramics based on high-throughput calculations is constructed. Six perovskite oxides are predicted as new thermal barrier coating materials based on the established property database of perovskites.

1. Introduction

The ABO_3 perovskites, a family of compounds having the same structure with $CaTiO_3$, have been intensively studied since the middle of the twentieth century. An ideal perovskite crystallized in the $Pm\bar{3}m$ group has cubic symmetry, with A cations occupying the body center, B cations the vertices and O anions on the middle of edges (Figure 1(a)). Due to the large variability in A and B cations and the subsequent interplay of structural, magnetic and transport related properties, a wide range of excellent physical/chemical properties including electro-optical effects, piezo-, ferro- and pyroelectricity,

are commonly observed in this family [1,2]. As such, they have been proposed as electronic, magnetic, structural and refractory materials for various applications [3–5]. Meanwhile, perovskite oxides with low thermal conductivities and good mechanical properties also meet the crucial performance requirements for TBC (thermal barrier coating) materials.

TBCs are ceramic coatings deposited onto the surface of gas turbine blades used in the hottest section of gas turbine engines to protect the superalloy substrate from the hot-gas stream [6]. The critical function of TBCs demands materials that simultaneously have low

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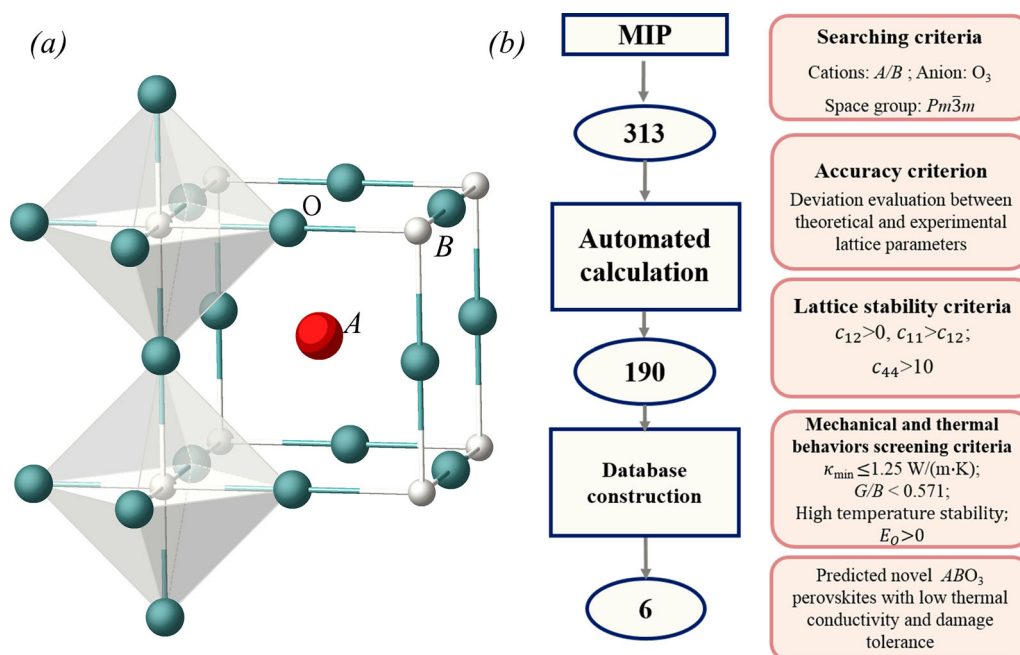


Figure 1. (a) The crystal structure of ABO_3 perovskite. (b) Workflow of automated calculations and criteria for data screening. 313 ABO_3 perovskites collected from MIP are set up as the initial materials for the automated calculations. 190 perovskites are identified as stable structures referring to the convergence and lattice stability criteria; meanwhile their mechanical and thermal properties are catalogued in database. At last, 6 materials are identified as promising TBC materials.

thermal conductivity and sustainable mechanical behavior (i.e. good damage tolerance) during thermal cycling under severe operating conditions. The current commercial TBC material YSZ (Y_2O_3 partially stabilized ZrO_2) has an application temperature limit of 1200°C and therefore cannot be used for the next generation of gas turbine engines with higher operating temperatures. Perovskites are a promising alternative for extremely high temperature TBC applications [7], as experimental thermal conductivities can be as low as $2.08 \text{ W/(m}\cdot\text{K)}$ for $SrZrO_3$ and $1.65 \text{ W/(m}\cdot\text{K)}$ for Yb_2O_3 doped $SrZrO_3$ at 1000°C [8–10]. However, the sparsity of data on mechanical and thermal properties of perovskites retard efforts towards realizing improved TBC materials. A grasp of the property distribution in perovskite oxide family and the construction of a proper screening strategy are necessary for accelerating the design and discovery of perovskite-based TBC materials.

As a burgeoning area of the material science [11–13], high-throughput screening facilitates the generation and analysis of large quantities of data in an efficient manner for the prediction and tailoring of novel material properties. Herein, high-throughput screening employing first-principles calculations is conducted to map the intrinsic performance of perovskites as possible TBC materials. A multiple selection criteria approach is proposed to screen the data rationally. Sequentially, a detailed database containing the theoretical mechanical

and thermal properties of 190 perovskites is established, which is available in Supplementary. Using this workflow, 6 ABO_3 perovskites with low minimum thermal conductivity and good intrinsic quasi-ductility are predicted as promising TBC materials. The predicted thermal barrier materials and the related strategies are expected to guide not only the future TBC material development but also the design of structural materials with desired mechanical and thermal properties.

2. Methods

Automatic calculations are performed via our developed code adopting Vienna *Ab initio* Simulation Package (VASP.5.4.4) based on density functional theory (DFT) [14]. The generalized-gradient approximation (GGA-PBEsol) [15] is used as the exchange correlation functional in this work due to its good reproduction of experimental perovskite structures [16]. A 500 eV cut-off energy and a $4 \times 4 \times 4$ k -points mesh over Brillouin zone (BZ) in Morhorst-Pack method are adopted [17]. Spin polarization is taken into account in all calculations. The convergence criterion is that the forces on individual atoms are less than $5 \times 10^{-3} \text{ eV/\AA}$. The second order elastic constants are calculated by generating four distorted unit cell structures for each strain pattern under the maximum strain amplitude of 0.4% . The mechanical properties are calculated using Voigt-Reuss-Hill

approximation [18–20] and the minimum thermal conductivity $\kappa_{\min}$ is calculated employing Clarke's model that refers to the lowest limit of thermal conductivity at high temperatures [21–23]. The defect formation energy of oxygen vacancy E_O is calculated by $E_O = E_d - E_p + \mu_O$, where E_d is the total energy of the supercell with the oxygen vacancy and E_p the total energy of the perfect supercell. μ_O is the chemical potential of oxygen defined as $\frac{1}{2}$ of the total energy of O_2 . All ABO_3 structures are obtained from MIP (Materials Informatics Platform) [24] that is a newly established repository with the ability of automated high-throughput calculations. All the structures are optimized in the automated workflow before further property evaluations.

3. Results and discussion

3.1. The multiple selection criteria approach and property database

The multiple selection criteria approach in the framework consists of four parts: (1) search settings to traverse the MIP, (2) the convergence criterion for structural optimization with an accuracy judgment of the calculation results, (3) lattice stability criteria for the perovskite structure screening and (4) criteria for the prediction of the perovskite TBC materials. The investigation strategy constructed in this work covers the entire process from the multi-criteria system to the terminal material prediction. The multiple filters are designed to implement the data check and error detection, which are supposed to spur further comprehensive studies for the structural ceramic development.

3.2. Initial material selection

313 ABO_3 compounds were selected from the MIP following the search settings given in Figure 1(b). The convergence criterion of the structural optimization (as described below) evaluates the reliability of the structures within the DFT framework. As a quick evaluation, we employ 5 atom cubic unit cells for the high-throughput calculations at this stage. The credibility of the theoretical results is checked by comparing the calculated lattice parameters with available experimental data in ICSD [25,26], as illustrated in Figure 2. Deviations between the calculated and experimental values are quite low, with an average value of 1.63% (see Supplementary Table S1). The satisfactory reproducibility demonstrates the reliability of our DFT calculation strategy.

3.3. Mechanical stability selection criteria

The elastic tensor reflects the structural response to a given stress and/or strain. As it closely correlates to

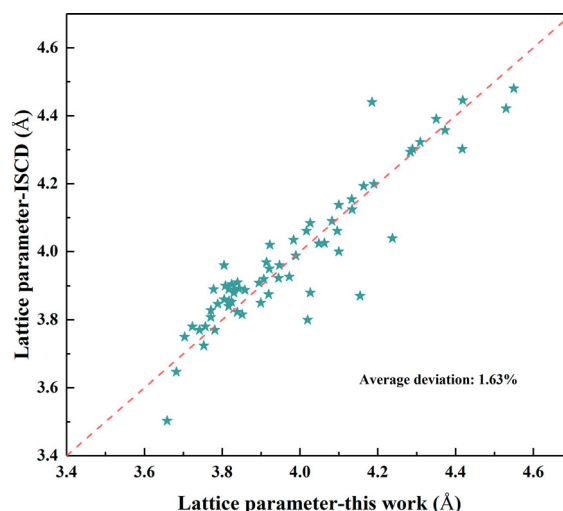


Figure 2. Available experimental lattice parameters from ICSD in comparison with the theoretical data calculated in this work.

the natural characteristics of materials and governs the mechanical properties, the second order elastic constant is accepted as a critical descriptor for the prediction and design of materials with expected mechanical/thermal properties [27]. However, experimental measurements of second order elastic constants are difficult because of the lack of single crystal samples and therefore only a small amount of experimental elastic constants are available in existing databases, which impede the exploration of materials with desired properties. Here, the second order elastic tensors (c_{11} , c_{12} and c_{44}) of perovskites are generated from DFT calculations in the high-throughput framework after structural optimization. The lattice stability criteria based on second order elastic constants are defined as (1) $c_{12} > 0$, $c_{11} > c_{12}$ and (2) $c_{44} > 10$. The lattice stability filter (1) refers to the Born-Huang stability criteria [28] that the aforementioned two conditions have to be fulfilled for the cubic lattice to be stable. Filter (2) is our empirical criterion considering the structural stability of TBC candidates at high temperatures, where c_{44} corresponds to the resistance against shear deformations. Within the convergence and lattice stability criteria, 190 perovskites are found to possess good lattice stability. For each of these remaining structures, the intrinsic mechanical properties (bulk modulus B , shear modulus G , Young's modulus E , Zener constant Z and Poisson's ratio ν , etc.) are predicted (see Supplementary Table S2).

3.4. Thermal conductivity selection criteria

Since low thermal conductivity is the dominant metric for TBC materials, the prediction of thermal conductivities are quite significant for potential TBC material searching. The theoretical minimum thermal conductivity

is predicted based on the Clarke model [21,29]. For TBC applications, $\kappa_{\min} \leq 1.25 \text{ W/(m K)}$ is adopted as the cutoff after considering thermal conductivities of the widespread used TBCs, 1.2–1.8 W/(m K) for 7YSZ [10], 1.5 W/(m K) for $\text{La}_2\text{Zr}_2\text{O}_7$ [22] and 1.3 W/(m K) for $\text{Gd}_2\text{Zr}_2\text{O}_7$ [30]. We find a total of 86 structures with thermal conductivities lower than this cutoff. The thermal properties (Debye temperature Θ_D , the minimum thermal conductivity $\kappa_{\min}$, etc.) for the 190 perovskites are listed in Supplementary Table S2.

3.5. Initial selection of candidate TBC materials

When it comes to the prediction of new TBC materials, challenges for the overall mechanical and thermal properties of employed structural materials brought by the harsh operating environments in engines should be faced directly. The basic performance requirement for the material is to own low thermal conductivity, meanwhile it is also crucial to be damage tolerant for a prolonged service life. For a measure of damage tolerance, we employ a quasi-ductility requirement. Pugh's ratio defined as the ratio of shear modulus to bulk modulus G/B , is generally used for the prediction of the quasi-ductility of materials [31,32]. With a G/B beneath the boundary value of 0.571, materials tend to have good intrinsic quasi-ductility. As such, to identify materials suitable for TBC applications, we screen for perovskites with good damage tolerance ($G/B < 0.571$) and ultra-low minimum lattice thermal conductivity ($\kappa_{\min} \leq 1.25 \text{ W/(m K)}$). Figure 3 displays the property distribution of the 190 perovskites for the cross considered criteria of Pugh's ratio and thermal conductivity. Perovskites in the category II are predicted to be both quasi-ductile and have low thermal conductivity; thus narrowing the candidate pool to 79. Moreover, with the considerations of high temperature stability, perovskites composing of alkali metal elements or actinides in the aforementioned group are excluded. Finally, to eliminate materials that may have large electronic thermal conductivity, we omit materials with no band gap. This significantly reduces the candidate pool to 7 insulating perovskites.

3.6. Defect tolerance

A final check was performed to explore the oxygen vacancy formation energies, E_O , of the remaining 7 perovskites (in a $2 \times 2 \times 2$, 40-atom unit cell) was calculated with structure relax as described in the methods section. Surprisingly, only one of the structures BiScO_3 , was determined to be favorable to oxygen vacancy formation, $E_O = -2.94 \text{ eV}$, indicating the existence of a large amount of oxygen vacancies in BiScO_3 ultimately leading

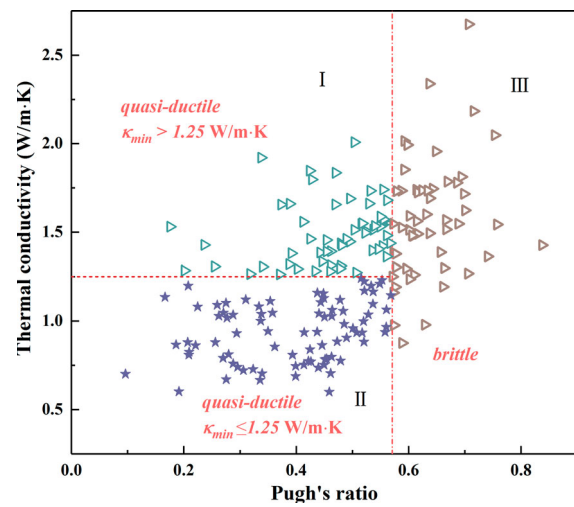


Figure 3. Pugh's ratio versus the minimum thermal conductivity of 190 ABO_3 perovskites.

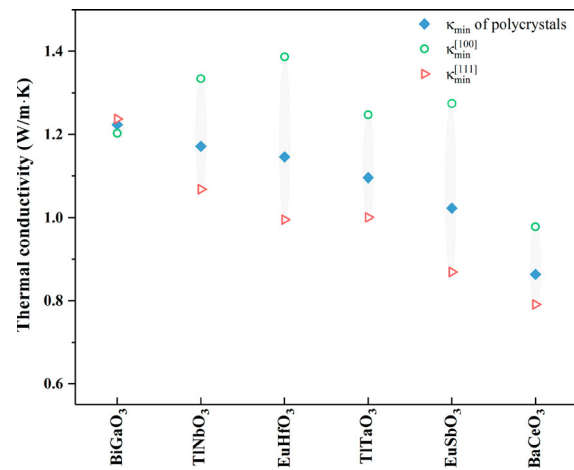


Figure 4. The minimum thermal conductivity of 6 predicted low thermal conductivity ABO_3 perovskites after considering the anisotropic nature.

to its structural degradation. The remaining six materials were found to be unstable to defect formations with positive formation energies of: 5.25 eV for BaCeO_3 , 2.38 eV for BiGaO_3 , 6.06 eV for EuHfO_3 , 0.61 eV for EuSbO_3 , 4.70 eV for TiNbO_3 and 5.78 eV for TiTaO_3 . These are predicted to have polycrystalline minimum thermal conductivity ranging from 0.86 to 1.22 W/(m K) (Figure 4). Together they are expected to possess structure stability, low thermal conductivity and mechanical stability, and should be ideal for application as novel TBC candidates.

Lastly, the intrinsic anisotropy nature of the predicted 6 perovskites is discussed. Figure 4 gives a holistic illustration on the anisotropic nature through comparing $\kappa_{\min}$ s of polycrystals with $\kappa_{\min}$ s along [100] ($\kappa_{\min}^{[100]}$) and [111] ($\kappa_{\min}^{[111]}$) directions. For the perovskite compounds with a Zener constant over 1, a decreased value

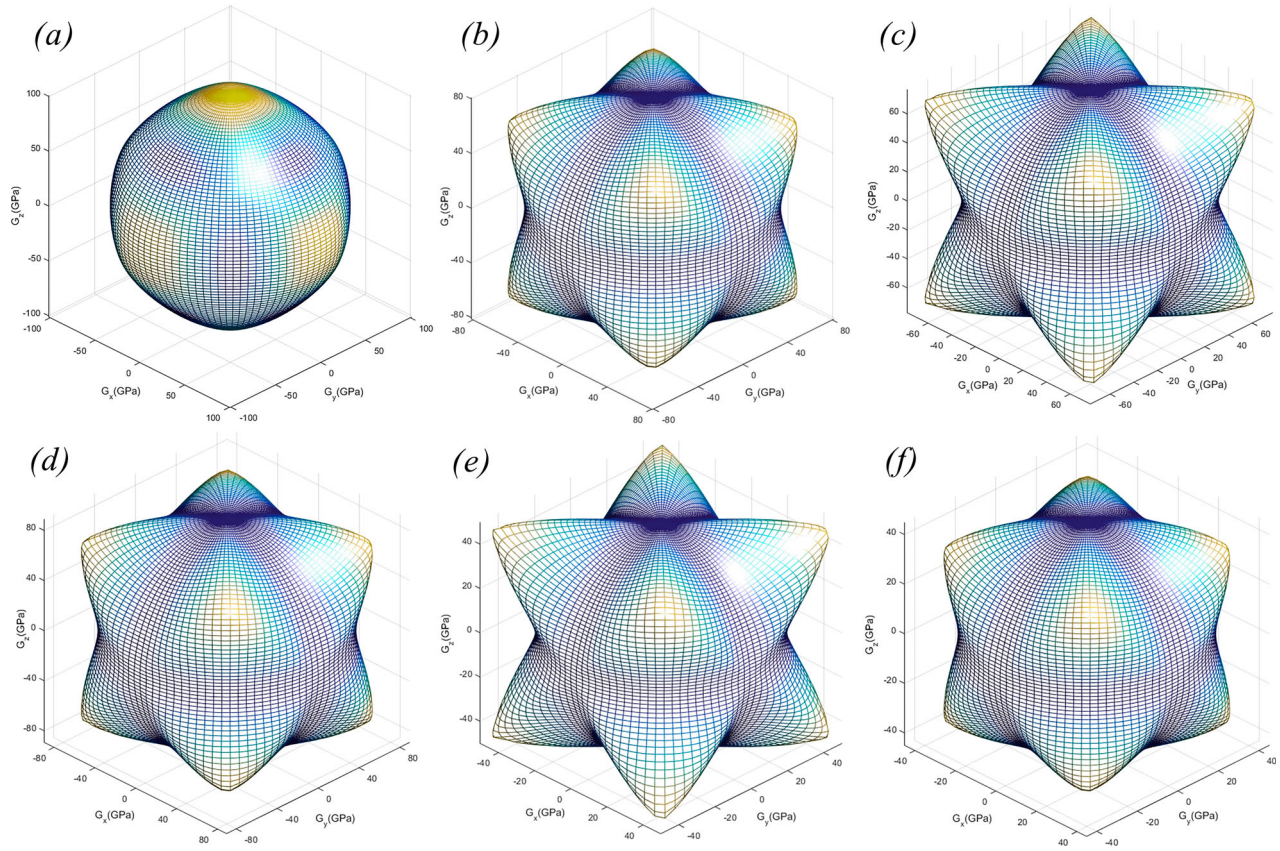


Figure 5. Minimum shear modulus $G_{\min}$ of (a) BiGaO₃, (b) TiNbO₃, (c) EuHfO₃, (d) TiTaO₃, (e) EuSbO₃ and (f) BaCeO₃.

of $\kappa_{\min}$ is reached in the [100] direction, otherwise the decreased $\kappa_{\min}$ is along the [111] direction. The polycrystalline minimum thermal conductivities of the predicted 6 perovskites range from 1.22 to 0.86 W/(m K). The anisotropic considerations bring decreased thermal conductivities up to 15.1%. The discrepancy between $\kappa_{\min}^{[100]}$ and $\kappa_{\min}^{[111]}$ exhibited as the gray shadow area in Figure 4 displays the tailorable ranges of the thermal conductivity. The mechanical/thermal properties of these 6 predicted ABO₃ perovskites as well as their anisotropic thermal behaviors are listed in Supplementary information Table S3. Figure 5 illustrates the directional dependent minimum shear moduli $G_{\min}$ of the 6 predicted perovskites. The directions with the lowest shear modulus suggest the most likely slip systems for the materials. For perovskites of BaCeO₃, EuHfO₃, EuSbO₃, TiNbO₃ and TiTaO₃, the minimum $G_{\min}$ are in the [100] direction on (110) planes, while the corresponding value of BiGaO₃ is in the [111] direction on (110) planes, manifesting that the slip system is [100] (110) for the former five perovskites but [111] (110) system for BiGaO₃. The knowledge on the direction-dependent shear performance is helpful in determining the slip systems of materials and analyzing the fracture or failure modes. Moreover, knowing the shear anisotropy is also important

in strengthening or weakening certain shear modes to tailoring the mechanical properties of perovskites.

In terms of experiments, the directional crystal growth has been achieved in many techniques. For examples, Arunkumar [33] disclosed that different annealing mechanisms of CeO₂ films deposited via EBPVD (Electron Beam Physical Vapor Deposition) are correlated with the texture growth of (111) planes. In our previous work, the growth orientation of lanthanum zirconate coatings prepared by LCVD (Laser Chemical Vapor Deposition) differs depending on whether the laser irradiation exists. The major growth orientation is [111] with 16 W/cm² laser irradiation assistance but [200] without laser irradiation [34]. The feasibility of directional growth provides a route for improving thermal barrier effects by designing the crystal growth orientation. In conclusion, the combination of material screening and the crystal growth orientation design will open a new perspective for the exploitation of promising thermal barrier materials.

4. Conclusions

In summary, high-throughput first-principles calculations with a multiple selection criteria approach were employed to predict perovskite-based materials suitable

for TBC applications. Six perovskites with the thermal conductivities below 1.25 W/(m K) and good damage tolerance are predicted as potential TBC materials. Our calculations further indicate that additional thermal barrier effects may be achieved through the orientation control during the deposition after considering their anisotropic nature. Subsequently, a mechanical and thermal property database containing 190 perovskite oxides was established, which is supportive of perovskite related studies. The investigation strategy, the established database and the predicted materials would be of great significance for accelerating the development of the structural and functional applications of ABO_3 and ABO_3 -based perovskite materials. It is expected this strategy could further enlighten following investigations of high-throughput screening for other functional material fields.

Disclosure statement

No potential conflict of interest was reported by the authors.

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