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Perspective

Multidimensional structural design of pioneer oxide ceramics with melting points above 3000 °C

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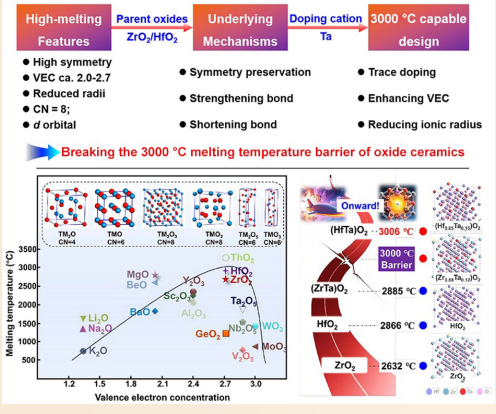
ABSTRACT: Thermal protective materials that remain stable above 3000 °C are crucial for hypersonic vehicles and nuclear fusion systems, yet reported nonradioactive oxides melt below this threshold. Zhou *et al.* demonstrated a cation engineering strategy that couples crystallographic symmetry, the coordination number, the valence electron concentration (VEC), the cation radius, and metal–oxygen bonding to increase the melting temperature of fluorite-type oxides. Guided by the above multidimensional design framework, Ta-doped HfO_2 was experimentally validated to have a melting point surpassing 3000 °C, which was confirmed as the first nonradioactive oxide with a melting point above 3000 °C. This perspective distills the underlying symmetry–VEC–bonding design principles and discusses how they can guide the discovery and engineering integration of ultrahigh-temperature oxide ceramics.



KEYWORDS: ultrahigh melting temperature; oxide ceramics; research paradigm; thermal protective materials

Main text: The essential needs of thermally protective materials that survive at temperatures > 3000 °C at hypersonic leading edges, propulsion hot sections, and plasma-facing components in nuclear fusion reactors significantly outweigh the melting temperatures (T_m) of available nonradioactive oxides, whose T_m values limit their ability to record [1]. Moreover, the conventional alloying and substitution strategies of oxides often depress T_m rather than increase it [2]. This persistent gap between application demands and intrinsic T_m has historically been addressed mainly through empirical alloying, with few examples where a clear, quantitative design logic successfully pushes T_m upward. In this context, Zhou *et al.* [3]. constructed a statistically established relationship between T_m and key material parameters in binary transition-metal oxides. They advanced a cation engineering approach that relates crystallographic symmetry, VEC, cationic size, and metal-oxygen bonding to elevated T_m, as summarized in Fig. 1. This development continues and extends the long-term work of the Zhou group on the first-principle guided design of high-temperature structural ceramics, in which electronic-structure descriptors and phase stability criteria are established for complex oxides and related multicomponent systems. The proposed relationship links the high T_m to high-symmetry structures with a coordination number (CN) of 8 [4], an optimal VEC window of 2.04–2.70, small cation radii shortening *M*–O bonds [5], and mixed ionic-covalent bonding facilitated by *d*–*p* orbital overlap. The 5*d* cations show relativistic 6 s contraction and 5*d* expansion to enhance orbital overlap [6,7]. Within the proposed framework, Ta provides one extra valence electron relative to Zr/Hf and a smaller radius [8]; subsequently, the high-symmetry structure is maintained, and the VEC and bonding strength are increased. These characteristics motivate Ta as a targeted dopant for ZrO_2/HfO_2 hosts, which perfectly satisfies the proposed high-melting-point structural criteria of oxide ceramics [9].

The implementation in $Zr_{1-x}Ta_xO_2$ and $Hf_{1-x}Ta_xO_2$ follows the proposed design logic. X-ray diffraction confirmed the single-phase solid solutions produced by high-temperature solid-state synthesis, and the phase constitution shifted toward higher-symmetry tetragonal/cubic polymorphs with increasing Ta content. The lattice contraction caused by substituting Ta^{5+} for Zr^{4+}/Hf^{4+} is reported in Ref. [3] because Ta^{5+} has a shorter ionic radius than Zr^{4+}/Hf^{4+} cations do [10]. The charge-density difference analysis indicates strong *d*–*p* hybridization, and UV-vis and electrical measurements reveal a higher Fermi level and a narrowed band gap for the $Zr_{1-x}Ta_xO_2$ and $Hf_{1-x}Ta_xO_2$ oxides. The bulk moduli of $Zr_{1-x}Ta_xO_2$ and $Hf_{1-x}Ta_xO_2$ increase with increasing Ta content, which serves as an indicator of increased bond strength and enables composition screening [11]. The

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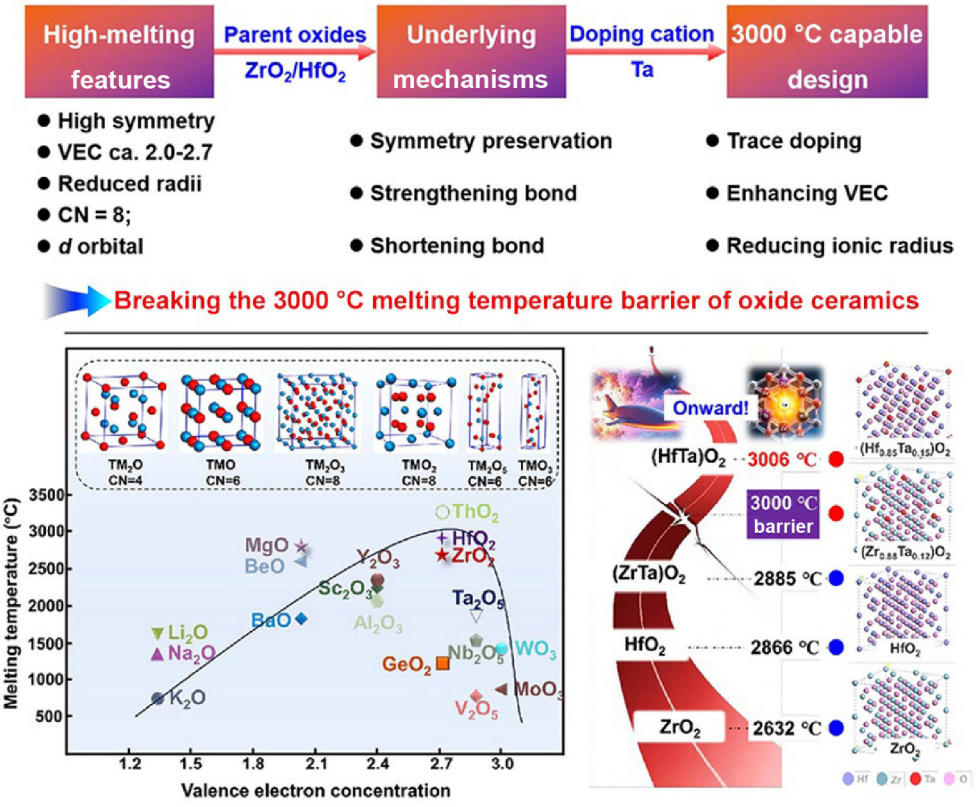

Fig. 1 Design criteria and verification process of high-melting-point oxide ceramics [3].

optimal compositions are $Zr_{0.88}Ta_{0.12}O_2$ and $Hf_{0.85}Ta_{0.15}O_2$ with T_m values of 2885 and 3006 °C, respectively, which are consistent with first-principles predictions and the empirical relationship of T_m = 607 + 9.3B [12]. In summary, these results provide a clear, data-driven basis for selecting candidate compositions for subsequent extreme-temperature melting tests.

Laser heating measurements have provided decisive metrics under explicit criteria of volumetric collapse and complete melting. The undoped oxides of ZrO_2 and HfO_2 with T_m values of 2632 and 2866 °C, respectively, are also measured as reference oxides, and significant increases in T_m are recorded for the optimized solid solutions of $Zr_{0.88}Ta_{0.12}O_2$ and $Hf_{0.85}Ta_{0.15}O_2$. These increases are unusual for oxide solid solutions, proving that adding a small amount of Ta cations with a high valence of 5*d* and short ionic radius and 8 CN can increase the T_m when high-symmetry crystals are preserved and that the VEC slightly increases.

Zhou's work established a coordinated symmetry-VEC-radius-CN-orbital strategy to increase the T_m of nonradioactive oxides above 3000 °C and expanded the design space for thermal protection systems across various application scenarios, as shown in Fig. 2. This study also outlines an actionable development route: (i) selecting high-symmetry, high-CN hosts; (ii) introducing small-radius, high-valence 5*d* dopants to increase the VEC in the effective range; (iii) using the bulk modulus as an indicator of bonding strength to prescreening oxide compositions with high T_m. The remaining challenges, such as oxidation resistance, volatilization, thermal shock tolerance, insulation performance, and resistance to spallation under cyclic high-enthalpy reactive flows, together with reliable lifetime assessment under realistic thermal and mechanical gradients, highlight future research directions. More effort is needed to motivate further progress, including atomic-scale studies of defects and melting mechanisms, systematic measurements of high-temperature mechanical and

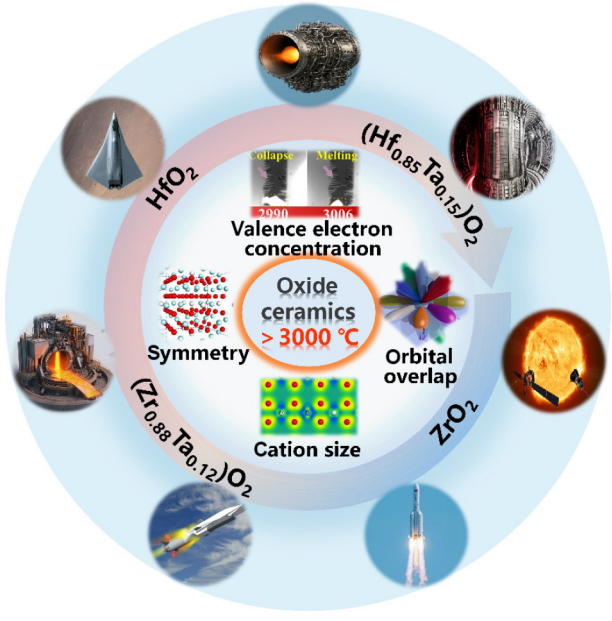

Fig. 2 Generalizable paradigm and application scenarios inspired by Ref. [3].

thermophysical properties, and engineering validation of coatings and multilayer architectures under simulated service environments. Additionally, high-throughput computation and machine learning-assisted material screening can further expand the compositional space concerning mixed anion or multielemental doping of Ta-based systems. Within this context, the symmetry-VEC-radius-CN-orbital framework can serve as a descriptor set for the design and optimization of ultrahigh-temperature oxides. The compositional design can guide the development of multication oxides with tailored melting points,

thermal expansion coefficients, and oxygen transport behavior. Thermal protective coatings can be used to design thermal and environmental barrier coatings that can tolerate relatively high gas temperatures, maintain phase stability, and resist ablation in oxygen- and steam-rich flows. For hot-end components, the same design logic can be extended to oxide-based structural ceramics and protective layers for turbine blades, vanes and hypersonic leading edges in oxygen-rich environments. In essence, this multidimensional structural design framework provides a clear route for translating high-T_m oxide ceramics into thermal protection materials, accelerates their deployment in extreme environments, and offers a general template for the discovery of new ultrahigh-T_m oxide families.

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Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article. The author Jing Feng is the Editorial Committee member of this journal.

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