

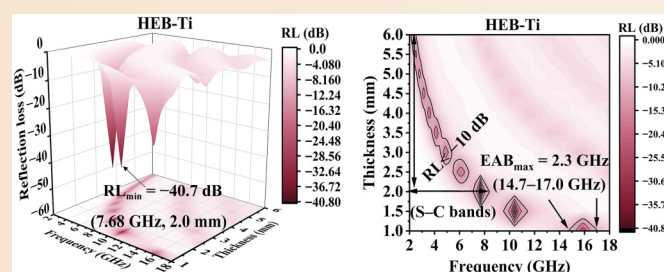
# Synthesis of novel high-entropy diborides with high-efficiency electromagnetic wave absorption and excellent thermal stability

Chencheng Liu<sup>1,2,†</sup>, Qingyun Chen<sup>1,†</sup>, Peng Sun<sup>3</sup>, Xingye Wang<sup>2,✉</sup>, Shuyi Zeng<sup>1</sup>, Qijie Chen<sup>1</sup>, Tong Zhu<sup>2</sup>, Yi Zhu<sup>2</sup>, Wenlong Zhang<sup>2</sup>, Hui Song<sup>2</sup>, Yuezhong Wang<sup>2,✉</sup>, Kazuhito Nishimura<sup>2</sup>, Huasong Liu<sup>3,✉</sup>, Nan Jiang<sup>2</sup>

**Cite this article:** Liu C, Chen Q, Sun P, et al. *J Adv Ceram* 2025, **14**(2): 9221030. <https://doi.org/10.26599/JAC.2025.9221030>

**ABSTRACT:** Ceramic materials have obvious advantages in thermal stability, but impedance mismatch limits their ability to attenuate electromagnetic (EM) waves. Herein, a novel series of high-entropy  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti$ , and  $Hf$ ) ceramics were successfully synthesized via ultrafast high-temperature sintering (UHS) apparatus based on joule heating. The results indicated that the effect of high-entropy component on the magnetic loss of the system was relatively small, but the effect on the dielectric loss was larger. Among them, the  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}Ti_{0.2})B_2$  (HEB-Ti) sample demonstrated superior absorbing properties due to relatively moderate dielectric loss and optimal EM impedance matching. Moreover, because of its relatively moderate attenuation constant, it could achieve the maximum penetration of the EM wave and the minimum reflection after absorbing wave. As a result, the minimum reflection loss ( $RL_{min}$ ) was as low as  $-40.7$  dB, and the effective absorption band covered the entire low-frequency range from 2 to 8 GHz. Its excellent absorption performance was mainly due to the synergistic effect of various dielectric attenuation mechanisms, including defect polarization, dipole polarization, and conduction loss. Furthermore, thermogravimetric (TG) analysis showed that the sample exhibited excellent thermal stability and could withstand temperatures up to  $550$  °C in air and  $1000$  °C in an argon gas environment. The relevant work could provide meaningful references for the design of new high-performance ceramic wave-absorbing materials.

**KEYWORDS:** high-entropy diborides (HEBs); ultrafast high-temperature sintering (UHS); electromagnetic (EM) wave absorption; impedance matching



## 1 Introduction

The radar stealth capability of high-temperature components in advanced aircraft necessitates the development of electromagnetic (EM) wave-absorbing materials with exceptional thermal stability [1–3]. Currently, EM absorbing materials mainly include magnetic materials (ferrites [4,5], magnetic metals [6,7], etc.) and carbon-based materials (graphene [8], carbon nanotubes [9], etc.). Magnetic materials are prone to magnetic loss and decreased absorption performance at high temperatures. Carbon-based materials suffer from insufficient oxidation resistance in high-temperature aerobic environments, significantly reducing their

ability to attenuate EM waves. Ceramic materials are ideal microwave absorbing materials that can be served in extreme environments due to good antioxidation properties and excellent chemical corrosion resistance [10]. Among ceramic materials, high-entropy diborides (HEBs) have garnered significant attention because of their tunable electrical conductivity and excellent chemical stability [11–14]. However, achieving an optimal balance between oxidation resistance and EM wave absorption for HEBs remains a significant challenge.

In high-temperature environments, oxidation resistance plays a critical role in ensuring the long-term stability of materials. Previous studies have shown that the multielement alloying effect

† Chencheng Liu and Qingyun Chen contributed equally to this work.

<sup>1</sup> College of Physics and Electronic Information Engineering, Guilin University of Technology, Guilin 541004, China. <sup>2</sup> State Key Laboratory of Advanced Marine Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China. <sup>3</sup> Tianjin Key Laboratory of Optical Thin Films, Tianjin Jinhang Technical Physics Institute, Tianjin 300308, China.

✉ Corresponding authors. E-mail: X. Wang, [xingyema\\_wang@163.com](mailto:xingyema_wang@163.com); Y. Wang, [wangyuezhong@nimte.ac.cn](mailto:wangyuezhong@nimte.ac.cn); H. Liu, [liuhuasong@yeah.net](mailto:liuhuasong@yeah.net)

Received: October 18, 2024; Revised: December 23, 2024; Accepted: January 6, 2025

© The Author(s) 2025. This is an open access article under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0, <http://creativecommons.org/licenses/by/4.0/>).

in HEBs enabled these materials to exhibit remarkable stability, providing a unique advantage in high-temperature applications. For example, Tallarita *et al.* [15] reported that  $(\text{Hf}_{0.2}\text{Mo}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2})\text{B}_2$  demonstrated an exceptionally low oxidation weight gain rate at temperatures as high as 1473 K, significantly outperforming its individual diboride components, such as  $\text{TiB}_2$ ,  $\text{HfB}_2$ , and  $\text{TaB}_2$ . Similarly, Guo *et al.* [16] reported that  $(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2})\text{B}_2$  exhibited superior oxidation resistance up to 1400 °C, surpassing the performance of most constituent metal diborides, including  $\text{TiB}_2$ ,  $\text{CrB}_2$ ,  $\text{ZrB}_2$ ,  $\text{NbB}_2$ , and  $\text{TaB}_2$ . Despite the promising high-temperature stability of HEBs, their EM wave absorption properties are often affected by the formation of oxide layers under high-temperature conditions. Related studies have indicated that as the temperature increased, the EM wave absorbing properties of materials can be significantly altered. For example, Qiao *et al.* [17] systematically investigated the EM wave absorption properties of high-entropy  $(\text{Mo}_{0.25}\text{Cr}_{0.25}\text{Ti}_{0.25}\text{V}_{0.25})_3\text{AlC}_2$  (MCTV) after oxidation at various temperatures, ranging from room temperature to 800 °C. The results revealed that the EM wave absorption behavior of the MCTV-600 and MCTV-800 samples differed significantly from that of the MCTV and MCTV-400 samples, primarily because of phase composition changes. Specifically, as the temperature increased, oxide layers progressively formed on the material surface. The formation of oxide layers significantly affects the EM properties, particularly by altering the conductivity and dielectric constant. These issues were critical parameters to influence the EM wave absorption. Therefore, achieving excellent EM wave absorption and thermal stability in HEBs is highly important.

However, the EM wave attenuation capacity of most absorbers utilizing HEBs is restricted because of their impedance mismatch. Recent studies have demonstrated that component modulation can effectively enhance the EM wave absorption performance of materials. For example, Wang *et al.* [18] synthesized carbonized cellulose paper/HEAs- $\text{Mn}_{2.15}$  with emblematic shell-core heterointerfaces by manipulating the molar ratio of the component elements. Its minimum reflection loss reached −51.35 dB at an ultrathin thickness of 1.03 mm, achieving efficient EM wave absorption. Moreover, Cheng *et al.* [19] significantly improved the microwave absorption performance of polymetallic sulfide (PMS)/acetylene black (ACET) composites by modulating the ACET content. For HEBs, Zhang *et al.* [20] prepared an efficient and broadband EM wave absorbing material, high-entropy  $(\text{Cr}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta})\text{B}_2$ , with a minimum reflection loss of −56.2 dB at 8.48 GHz by incorporating Cr. Therefore, reasonable component modulation is expected to achieve excellent EM wave absorption performance and thermal stability for HEB.

HEBs show wide application potential due to the large composition adjustable space. At present, the most studied system of HEBs were  $(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{B}_2$  series [21–25]. Therefore, completing the study of HEBs with different

components is highly important. However, studies on HEBs containing the  $\text{VB}_2$  phase are scarce [26,27], which may be related to the fact that the introduction of V increases the difficulty of single-phase solid-solution formation. To mitigate these issues, three novel  $\text{VB}_2$ -containing high-entropy  $(\text{V}_{0.2}\text{Nb}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{X}_{0.2})\text{B}_2$  ( $\text{X} = \text{Mo}, \text{Ti}, \text{and Hf}$ ) materials were prepared in this work. Among them, Mo, Hf, and Ti were selected as variable elements, mainly on the basis of the following considerations: The introduction of Mo can significantly improve the electrical conductivity of the materials and then increase the dielectric constant of the materials to optimize its absorption performance in a specific frequency range. The introduction of Hf can improve the thermal stability and oxidation resistance, and its good electrical conductivity also plays an important role in enhancing the absorption capacity of EM waves. The introduction of Ti can improve the conductivity and oxidation resistance of the materials, which is expected to synergistically improve the absorption performance and thermal stability.

This work utilized the ultrafast high-temperature sintering (UHS) method to prepare three novel high-entropy  $(\text{V}_{0.2}\text{Nb}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{X}_{0.2})\text{B}_2$  ( $\text{X} = \text{Mo}, \text{Ti}, \text{and Hf}$ ) materials. By adjusting the components and triggering various EM loss mechanisms, such as defect polarization, dipole polarization, and conduction loss, the EM wave absorption performance of the  $(\text{V}_{0.2}\text{Nb}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{X}_{0.2})\text{B}_2$  system was improved. The  $(\text{V}_{0.2}\text{Nb}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2})\text{B}_2$  (HEB-Ti) sample exhibited excellent EM wave absorption performance. Its maximum EAB covered the entire low-frequency range from 2 to 8 GHz, and the  $\text{RL}_{\min}$  can reach −40.7 dB at 7.68 GHz with a thickness of 2.0 mm. In addition, the materials exhibited excellent thermal stability and can withstand temperatures up to 550 °C in air and temperatures up to 1000 °C in an argon gas environment. Related studies could provide important reference for the preparation and development of EM wave-absorbing materials in high-temperature environments.

## 2 Experimental

### 2.1 Material selection

Commercially available transition metal powders (involving V, Nb, Ta, Zr, Mo, Ti, and Hf) and amorphous boron powders were used as raw materials. The detailed information of the raw powder materials is listed in Table 1.

### 2.2 Material preparation

Ultrafast high-temperature sintering (UHS) is an innovative sintering method that can efficiently and rapidly prepare high-performance materials. It has significant features such as a uniform temperature distribution, high heating and cooling rates, and high sintering temperatures [28]. This rapid heat treatment can effectively prevent phase separation and excessive grain

**Table 1** Detailed information on raw materials

| Raw material | Detailed information                                                                                    |
|--------------|---------------------------------------------------------------------------------------------------------|
| V            | Purity: 99.9%, particle size: 100–200 mesh, Shanghai Aladding Biochemical Technology Co., Ltd., China   |
| Nb           | Purity: 99.8%, particle size: < 45 μm, Shanghai Aladding Biochemical Technology Co., Ltd., China        |
| Zr           | Purity: 99.9%, particle size: 15–53 μm, Shenzhen Jin Titanium New Material Technology Co., Ltd., China  |
| Ta           | Purity: 99.9%, particle size: 53–150 μm, Shenzhen Jin Titanium New Material Technology Co., Ltd., China |
| Mo           | Purity: 99.99%, particle size: < 100 μm, Shanghai Aladding Biochemical Technology Co., Ltd., China      |
| Ti           | Purity: 99.98%, particle size: < 45 μm, Shanghai Aladding Biochemical Technology Co., Ltd., China       |
| Hf           | Purity: 99.9%, particle size: 20–63 μm, Shenzhen Jin Titanium New Material Technology Co., Ltd., China  |
| B            | Purity: 99%, particle size: ≤ 20 μm, Shanghai Aladding Biochemical Technology Co., Ltd., China          |

growth and control the chemical composition and microstructure, thereby improving the material properties [29,30].

In the experiment, three new types of high-entropy ( $V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2}$ )B<sub>2</sub> (X = Mo, Ti, and Hf) were prepared via a UHS apparatus (1030D, Shenzhen Zhongke Jingyan Technology Co., Ltd., China), and the detailed preparation process is shown in Fig. 1. First, these transition metal powders were equimolarly weighed and then well mixed with 20% excess boron powder according to the ratio of the reaction equation [31]. Detailed information on the molar ratios of the raw reactants is listed in Table 2. The transition metal powders and boron powders were then mixed and ground by hand in an agate mortar for 6 h. Afterward, the mixed powders were pressed into a green body of  $\phi 10$  mm in diameter with a pressure of 10 MPa for 1 min. The green body was then placed between two pellets of the graphite heater of the UHS apparatus. An alternating current was subsequently applied to both ends of the pellets to heat the samples to 1900 °C within seconds under the protection of argon gas. During this process, borothermal reduction occurred. The temperatures were measured by an infrared radiation thermometer (E1RH, Fluke, USA). After the samples were heated at 1900 °C for 10 min, the current was subsequently decreased, allowing the samples to cool to ambient temperature. The as-obtained samples were collected and then ground into powders for subsequent testing.

### 2.3 Material characterization

The phase composition of the samples was tested via a powder X-ray diffractometer (PXRD; Advance D8, Bruker, USA) using Cu K $\alpha$  radiation. The surface compositions were analyzed via an X-ray photoelectron spectroscope (XPS; ESCALAB 250XI, Thermo Fisher Scientific, USA). The morphology and elemental distributions were investigated by a scanning electron microscope (SEM; Regulus 8230, Hitachi, Japan) with an energy-dispersive spectrometer (EDS) system and a transmission electron microscope (TEM; Talos F200X, Thermo Scientific, USA).

Vacancy defect information was obtained via an electron paramagnetic resonance (EPR; EMXplus-6/1, Bruker, USA). The thermal stability of the samples in air and Ar was evaluated via a thermogravimetric analyzer (TG; 209F1, Netzsch, Germany). The EM parameters from 2 to 18 GHz were measured via a vector network analyzer (N5234A, Agilent, USA). Before the measurement, each sample and paraffin wax were mixed at a mass ratio of 7:3 and compacted into a toroidal shape ( $\phi_{out} = 7.00$  mm,  $\phi_{in} = 3.04$  mm). Paraffin was used as the matrix materials to determine the real EM wave absorption capacity because the paraffin framework was lossless for incident EM waves [32].

## 3 Results and discussion

### 3.1 Phase composition and microstructure

Figure 2 shows the typical XRD patterns of ( $V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2}$ )B<sub>2</sub> (X = Mo, Ti, and Hf) and the variation in the diffraction peaks of the (111), (110), and (101) crystal planes. As shown in Fig. 2(a), all samples exhibited similar diffraction peaks in the range of 10°–90°. These diffraction peaks corresponded to the AlB<sub>2</sub>-type (*P6/mmm* spatial group) phase, which is consistent with the results reported by Liu *et al.* [23]. No diffraction peaks of oxide impurities were observed in any of the samples, indicating that they were single-phase solid solutions. An analysis of the (111), (110), and (101) diffraction peaks depicted in Fig. 2(b) revealed that the peak positions shifted to different degrees. Compared with the peak position of HEB-Mo, there was no significant shift in the peak position of HEB-Ti. In contrast, the peak position of HEB-Hf shifted to the left by approximately 0.9°. The difference in peak position was caused mainly by the different atomic radii of Mo, Ti, and Hf. A larger atomic radius increased the lattice spacing (*d*) [33]. The Bragg equation showed that when the lattice spacing (*d*) was larger, the angle 2 $\theta$  was smaller [34]. The atomic radii of Mo, Ti, and Hf were 1.40, 1.45, and 1.59, respectively [35]. Therefore, the peak position shift of HEB-Hf was

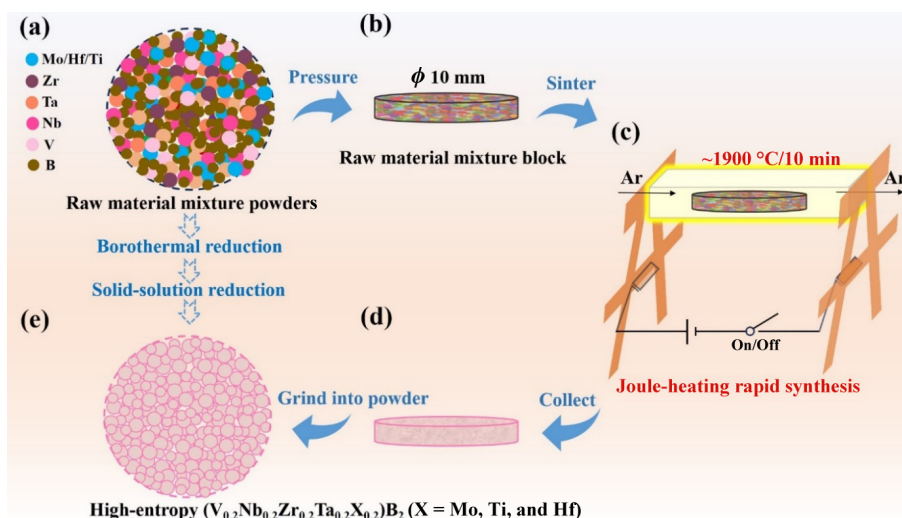


Fig. 1 Schematic diagram of preparation route for high-entropy ( $V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2}$ )B<sub>2</sub> (X = Mo, Ti, and Hf).

Table 2 Constituents of raw materials used for synthesizing ( $V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2}$ )B<sub>2</sub> (X = Mo, Ti, and Hf) and their corresponding sample codes

| Sample code | Composition                                                 | Molar ratio of raw reactant               |
|-------------|-------------------------------------------------------------|-------------------------------------------|
| HEB-Mo      | ( $V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}Mo_{0.2}$ )B <sub>2</sub> | V:Nb:Zr:Ta:Mo:B = 0.2:0.2:0.2:0.2:0.2:1.2 |
| HEB-Ti      | ( $V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}Ti_{0.2}$ )B <sub>2</sub> | V:Nb:Zr:Ta:Ti:B = 0.2:0.2:0.2:0.2:0.2:1.2 |
| HEB-Hf      | ( $V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}Hf_{0.2}$ )B <sub>2</sub> | V:Nb:Zr:Ta:Hf:B = 0.2:0.2:0.2:0.2:0.2:1.2 |

more significant than that of HEB-Ti. Overall, the change in the XRD peak may be related to various defects, such as lattice distortion, dislocations, and vacancies, which are introduced by heteroatom doping and high-temperature synthesis processes.

To further investigate the elemental composition, the as-synthesized samples were analyzed via XPS. As shown in Fig. 3(a), the full XPS spectra of HEB-Mo, HEB-Ti, and HEB-Hf samples revealed the presence of five different transition metal elements. Specifically, the HEB-Mo sample contained V, Nb, Ta, Zr, and Mo. The HEB-Ti sample contained V, Nb, Ta, Zr, and Ti. The HEB-Hf samples contained V, Nb, Ta, Zr, and Hf. These results further confirmed the successful synthesis of the high-entropy  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) system. The high-resolution V 2p, Nb 3d, Ta 4f, Zr 3d, and B 1s spectra were further analyzed to assess the influence of Mo, Ti, and Hf on the surface chemical states of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$ . As shown in Figs. 3(b)–3(f), the XPS peaks corresponding to V 2p, Nb 3d, Ta 4f, Zr 3d, and B 1s all shifted toward lower binding energies, indicating changes in the chemical state of the surface elements. This shift indicated an increase in the electron density around the atoms, which may influence the lattice constants [36]. According to the XRD results, an increase in the radius of doped atoms can lead to local lattice expansion, altering the electronic environment of the surrounding atoms and potentially inducing lattice distortion. The

observed shift of the XPS peaks toward lower binding energies was consistent with the peak shift to lower angles in the XRD patterns. These results further indicated that variations in the high-entropy components induced structural modifications within the material system.

Figures 4(a)–4(c) show the morphology of all the as-synthesized samples. There were irregularly shaped particles and agglomerates in all the samples. With the change in component element content, the grain size clearly increased, accompanied by increased porosity. The formation of intragranular pores may be attributed to rapid grain growth during the sintering process. In this scenario, the migration rate of the grain boundaries was faster than that of the pores, leading to the retention of the pores within the grains [37]. Notably, the presence of appropriate pores in HEB-Ti can improve interface impedance matching, ensuring that more EM waves can enter the materials and be absorbed rather than reflected [38]. The elemental distribution of the samples was characterized via SEM with EDS. As shown in Figs. 4(d)–4(f), the five metal elements in all the samples were homogeneously distributed at the micrometer scale. In addition, no elemental segregation could be observed in the entire scanning area, indicating good element distributions of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ). Combining the XRD and SEM-EDS analyses, it could be concluded that single-phase

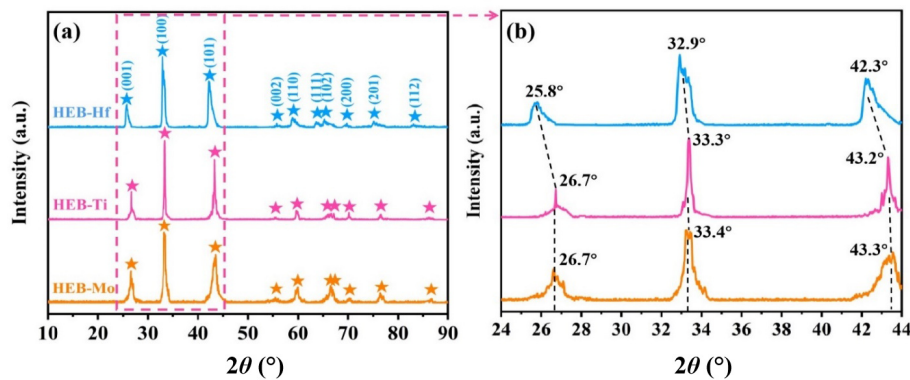


Fig. 2 (a, b) XRD patterns of samples and their diffraction peaks corresponding to (111), (110), and (101) crystal planes.

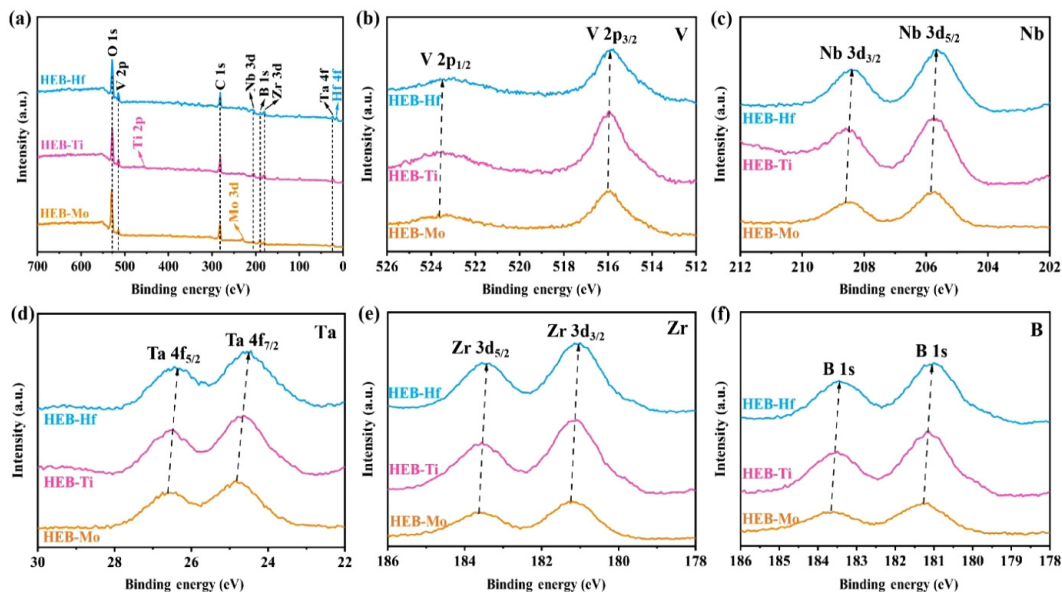


Fig. 3 (a) Full XPS spectra of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) and the corresponding high-resolution XPS spectra for (b) V 2p, (c) Nb 3d, (d) Ta 4f, (e) Zr 3d, and (f) B 1s.

$(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) ceramics with different pore numbers were successfully prepared via component modulation and UHS methods.

The microstructure evolution of the samples was further analyzed via high-resolution TEM (HRTEM), as shown in Figs. 5(a)–5(c). The  $d$ -spacings of the (100) lattice planes for HEB-Mo, HEB-Ti, and HEB-Hf were approximately 0.263, 0.265, and 0.269 nm, respectively. The results indicated that an increase in the atomic radius led to a corresponding increase in the lattice spacing ( $d$ ), which was consistent with the XRD results (Fig. 2(b)). The selected area electron diffraction (SAED) patterns with high symmetry shown in the insets of Figs. 5(a)–5(c) further confirmed the formation of hexagonal structures in all the samples. In addition, defects in the lattice, such as lattice stacking, deformation, disappearance, and point defects, gradually increase

with increasing atomic radius. These defects are caused by metal atoms with different radii and masses in high-entropy systems. Figures 5(d)–5(f) show the strong resonance peaks of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ), further indicating the formation of numerous dangling bonds and defects with unpaired electrons in the structure [39,40]. Compared with the HEB-Mo sample, the HEB-Ti and HEB-Hf samples presented stronger peak intensities. The introduction of Ti and Hf clearly caused the electronic transition, creating more dangling bonds and unpaired electrons. These dangling bonds and defects could act as dipole polarization centers to further enhance EM wave attenuation by inducing dipole polarization [41]. Overall, the pore structure and defect density of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) could be effectively controlled via modulation of the high-entropy component.

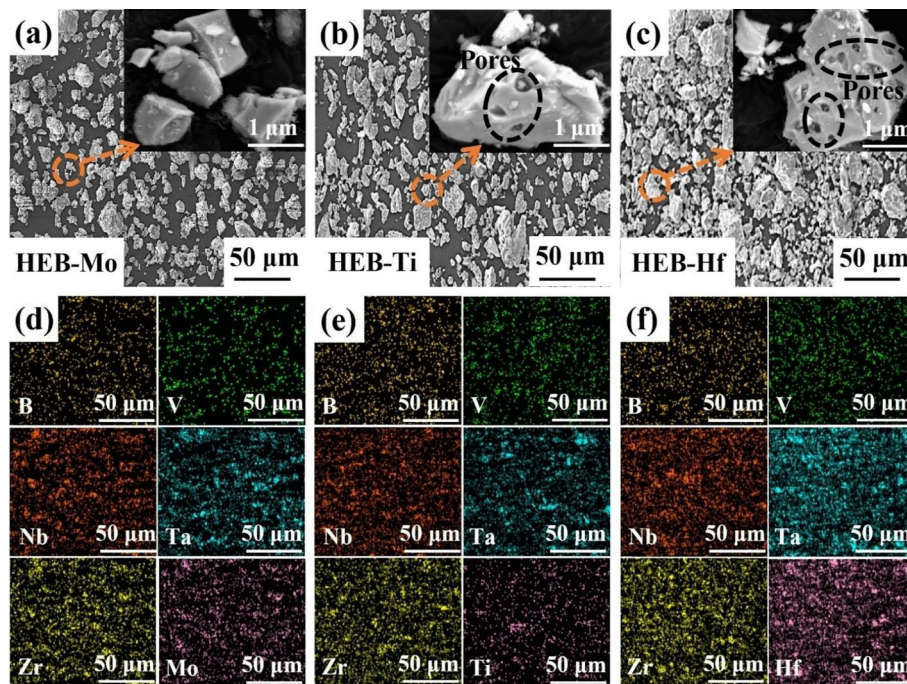


Fig. 4 (a–c) SEM images and (d–f) EDS maps of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ).

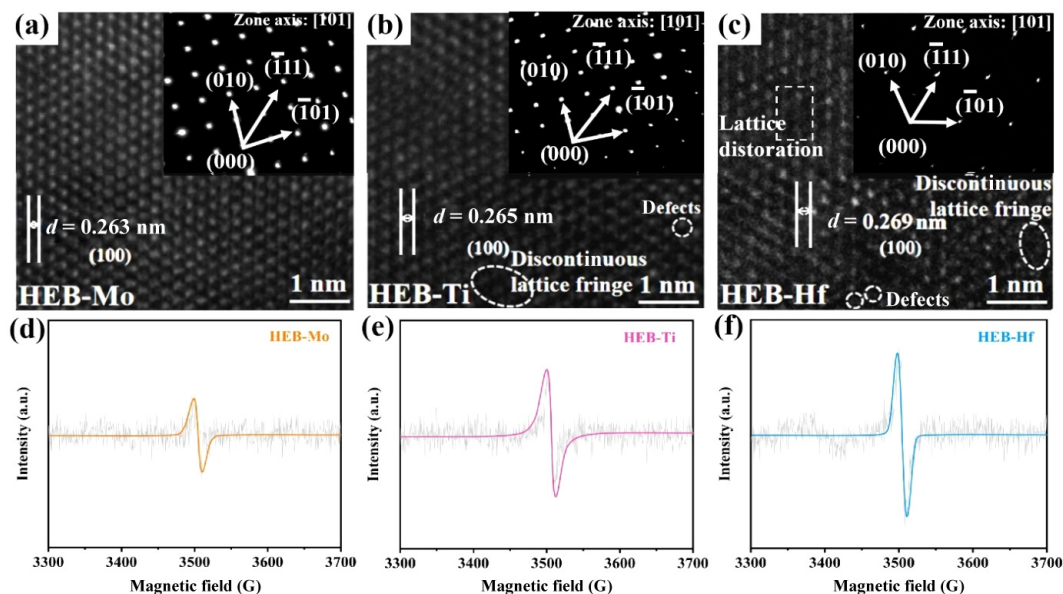
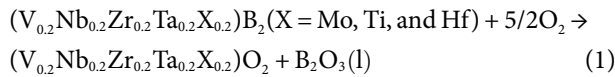


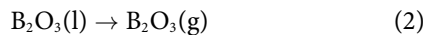
Fig. 5 (a–c) HRTEM images alongside SAED patterns and (d–f) EPR spectra of samples.

### 3.2 High-temperature stability

Figure 6 shows the TG curves of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) in both air and argon atmospheres, covering a temperature range from room temperature to 1000 °C. Under an air atmosphere (Fig. 6(a)), the mass of the HEB-Mo sample remained nearly unchanged until 490 °C. The masses of the HEB-Ti and HEB-Hf samples did not significantly change below 550 °C, indicating good thermal stability. In the temperature range from 550 to 800 °C, all the samples exhibited significant weight gain, which was attributed to high-temperature oxidation reactions, as described by Reaction (1) [42]:



The variation in weight gain rates among the samples indicated that the specific oxidation behavior was closely influenced by the material composition. Above 800 °C, the weight gain rates of all the samples decreased significantly. This deceleration may be due to the formation of  $B_2O_3$  protective glassy layers that provide protection for the underlying sample from further oxidation to some extent [43]. At approximately 1000 °C, a slight decrease in the mass of all the samples was observed, possibly resulting from the gasification of the  $B_2O_3$  protective layer (Reaction (2)):



which led to the partial loss of this protective layer. In contrast, under an argon atmosphere (Fig. 6(b)), the mass of all the samples remained nearly unchanged over the entire temperature range (room temperature to 1000 °C), demonstrating their excellent high-temperature thermal stability in an inert atmosphere. In summary, the samples exhibited good thermal stability in air atmosphere, but high-temperature oxidation led to mass gain, followed by a slight decrease in mass near 1000 °C due to  $B_2O_3$  volatilization. Under an argon atmosphere, the samples maintained high thermal stability over the entire temperature range without significant mass changes, fully demonstrating their superior performance in an inert environment.

### 3.3 EM wave absorption performance

To evaluate the EM wave absorption capability, the reflection loss (RL) values of the samples were calculated via Eqs. (3) and (4) [44]:

$$RL = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (3)$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left( j \frac{2\pi f d \sqrt{\mu_r \epsilon_r}}{c} \right) \quad (4)$$

where  $Z_{in}$ ,  $Z_0$ ,  $\epsilon_r$ , and  $\mu_r$  denote the input characteristic impedance,

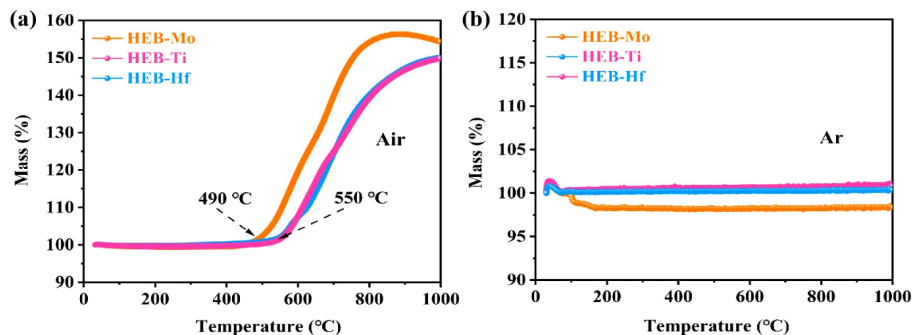


Fig. 6 TG curves of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) from room temperature to 1000 °C in (a) air and (b) argon.

free space impedance, relative complex permittivity, and relative complex permeability, respectively. Moreover,  $d$ ,  $c$ ,  $f$ , and  $j$  represent the absorber thickness, ray speed, frequency, and imaginary number units, respectively. In general, an RL value of  $-10$  dB means that 90% of the incident EM wave radiation is absorbed, and the corresponding bandwidth indicates an EAB [45].

Figure 7 shows the frequency dependence of the 3D RL plots and 2D color mapping of the EAB for HEB-Mo, HEB-Ti, and HEB-Hf. As shown in Figs. 7(a) and 7(b), HEB-Mo exhibited an  $RL_{min}$  of  $-11.3$  dB at 11.28 GHz with a thickness of 2.0 mm, and its maximum EAB was 0.7 GHz. In contrast, HEB-Ti demonstrated superior EM wave absorption performance, achieving an  $RL_{min}$  of  $-40.7$  dB at 7.68 GHz with a thickness of 2.0 mm and a maximum EAB of 2.3 GHz (Figs. 7(c) and 7(d)). For HEB-Hf, the  $RL_{min}$  reached  $-24.1$  dB at 12.64 GHz with a thickness of 1.5 mm, and the corresponding maximum EAB was 2.6 GHz (Figs. 7(e) and 7(f)). HEB-Ti clearly demonstrated the best overall EM wave absorption performance because of its low RL, wide EAB, and thinness. Overall, this study achieved tunable EM wave absorption in high-entropy  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) via modulation of the high-entropy component. According to SEM, TEM, and EPR analyses, component modulation can introduce defects that facilitate the establishment of polarization centers. This may be an important factor in optimizing impedance matching and improving the EM wave attenuation ability.

In addition, the  $1/4$  wavelength curves of all the samples were investigated. As shown in Figs. 8(a)–8(c), the RL peak of all samples shifted to a lower frequency with increasing absorption layer thickness ( $d_m$ ), which can be explained by the  $1/4$  wavelength matching theory (Eq. (5)) [46,47]:

$$d_m = \frac{nc}{4f_m \sqrt{|\mu_r| |\epsilon_r|}} \quad (5)$$

where  $n = 1, 3, 5, \dots$ , and  $d_m$ ,  $f_m$ ,  $\mu_r$ ,  $\epsilon_r$ , and  $c$  represent the matching thickness of the absorber, peak frequency, relative complex permeability, relative complex permittivity, and velocity of light ( $3 \times 10^8$  m/s), respectively. In addition, an RL value smaller than  $-4$  dB was generally considered a qualified value with an absorption coefficient ( $> 60\%$ ) in the low-frequency region because it was difficult to decouple the impedance matching and EM wave attenuation [48]. Notably, the RL values of HEB-Ti at 2–8 GHz were smaller than  $-10$  dB, indicating that its EAB covered the entire S–C band. Thus, it has significant advantages in terms of low-frequency absorption.

### 3.4 Comparison of EM wave absorption to that of other materials

We summarize the  $RL_{min}$  values and optimal EAB values of some

reported materials in Fig. 9. Jian *et al.* [49] noted that pure  $\text{ZrB}_2$  exhibited RL values greater than  $-5$  dB at a thickness range of 1–5 mm in the frequency range of 2–18 GHz. Song *et al.* [50] reported that  $\text{TiB}_2$  exhibited an  $\text{RL}_{\min}$  of  $-21$  dB at 8 GHz. Other materials, including TaC [51], SiC [52],  $\text{Ti}_3\text{C}_2$  [53],  $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{X}_{0.2})\text{C}$  ( $\text{X} = \text{Mo}, \text{Hf}, \text{and Cr}$ ) [54],  $(\text{Cr,Zr,Hf,Nb,Ta})\text{C}$  [55],  $\text{FeCoNiCrAl}$  [56],  $\text{LiZn FHM}$ s [57],  $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Mo}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{B}_2$  [58],  $(\text{Ti,Zr,Nb,Ta})\text{B}_2\text{-SiC}$  [59],

$\text{SiC/Si}_3\text{N}_4$  aerogels [60],  $\text{MoS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$  composites [61], and  $\text{NbS}_2/\text{PrGO}$  composites [62], demonstrated sufficiently low RL values, and their absorption was predominantly in the higher frequency range of 8–18 GHz. Conversely, our prepared HEB-Ti exhibited superior EM wave absorption in relatively low-frequency bands ( $< 8$  GHz). The maximum EAB of HEB-Ti covered the entire low-frequency range of 2–8 GHz. Its  $\text{RL}_{\min}$  reached as high as  $-40.7$  dB, demonstrating strong EM wave

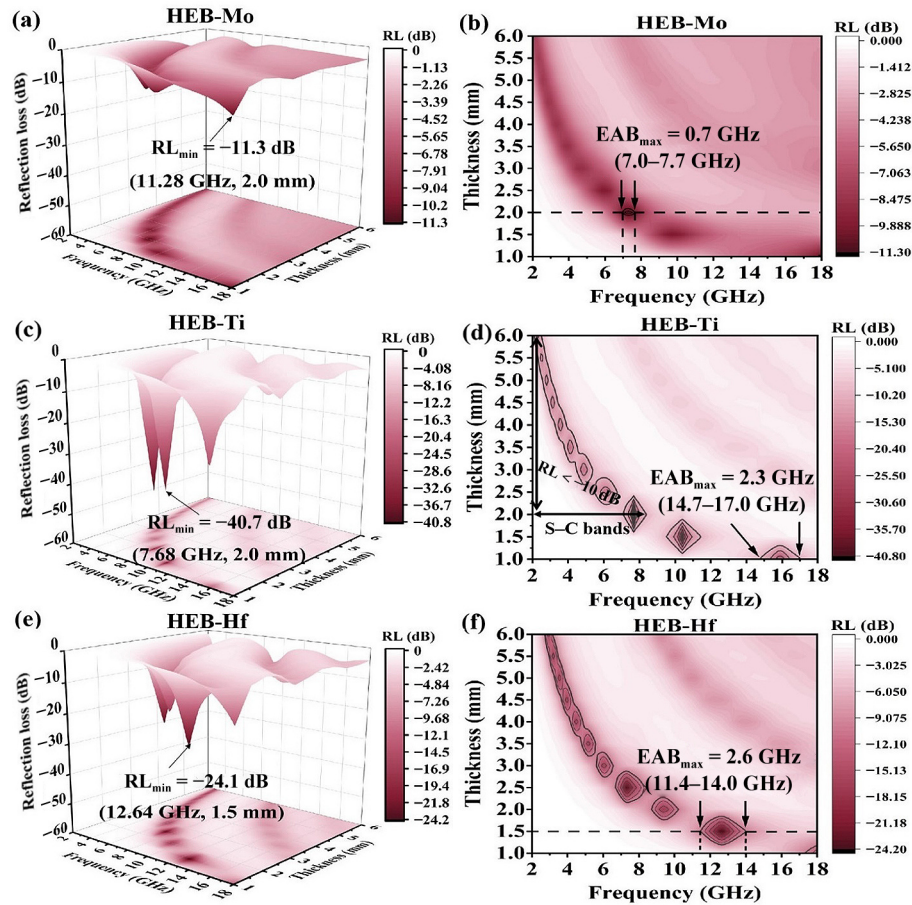


Fig. 7 Frequency dependence of 3D RL plots and 2D color mapping of EAB for (a, b) HEB-Mo, (c, d) HEB-Ti, and (e, f) HEB-Hf.

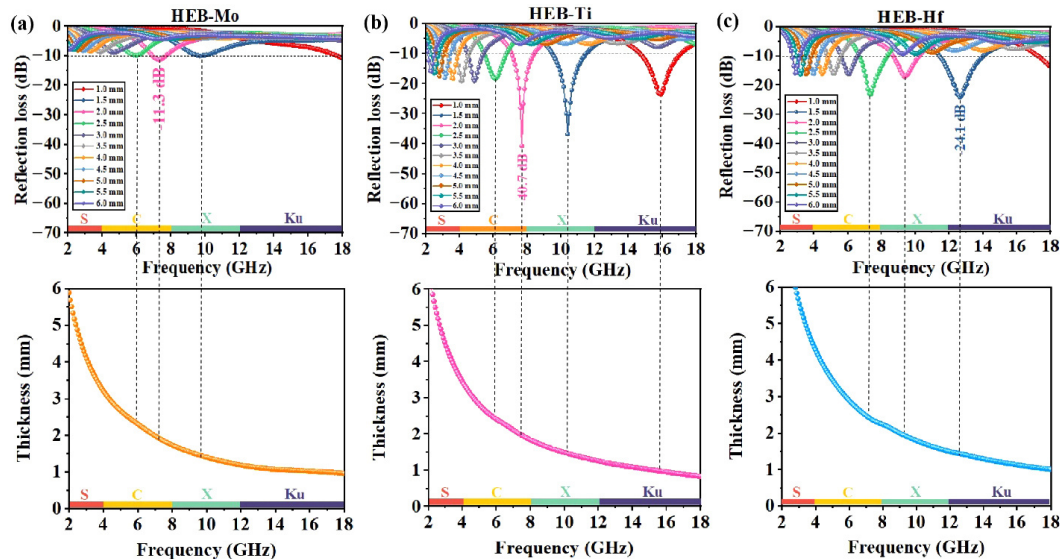


Fig. 8  $\lambda/4$  cancellation theory of (a) HEB-Mo, (b) HEB-Ti, and (c) HEB-Hf.

absorption capability. Comparative analysis suggested that the as-prepared HEB-Ti possessed great potential in the field of low-frequency EM wave absorption. This research thus provides valuable insights for advancing the development of high-performance ceramic wave-absorbing materials.

Typically, excellent impedance matching ( $|Z_{in}/Z_0|$ ) is an essential prerequisite for a good EM wave absorber. When the  $|Z_{in}/Z_0|$  value equals 1, EM waves can penetrate the surface of the materials without undergoing any reflection. As shown in Figs. 10(a)–10(c), the  $|Z_{in}/Z_0|$  values for HEB-Mo were significantly lower than 1, with a thickness range of 1.0–2.0 mm at a frequency of 2–18 GHz, indicating poor impedance matching. Conversely, both HEB-Ti and HEB-Hf achieved  $|Z_{in}/Z_0|$  values within the optimal range of 0.8–1.2 across the same frequency and thickness ranges. Specifically, the  $|Z_{in}/Z_0|$  values for HEB-Ti and HEB-Hf were 0.98 and 0.88, respectively, demonstrating their superior impedance matching performance compared with that of HEB-Mo. Furthermore, the results indicated that HEB-Ti exhibited better  $|Z_{in}/Z_0|$  characteristics than both HEB-Mo and

HEB-Hf did, underscoring its potential as a more effective EM wave absorber.

Another important parameter for comprehensively analyzing EM wave performance is the attenuation constant ( $\alpha$ ), which can be calculated via Eq. (6) [63]:

$$\alpha = \frac{\sqrt{2\pi f}}{c} \times \sqrt{\mu''\epsilon'' - \mu'\epsilon' + \sqrt{(\mu''\epsilon'' - \mu'\epsilon')^2 + (\mu'\epsilon'' - \mu''\epsilon')^2}} \quad (6)$$

A higher attenuation constant means that the material's ability to convert EM wave energy into other forms of energy is greater [64]. As shown in Fig. 10(d), the  $\alpha$  of HEB-Mo was greater than those of HEB-Ti and HEB-Hf. However, with respect to RL and EAB, HEB-Mo demonstrated the weakest EM wave absorption performance among the tested materials. The results showed that a high attenuation constant does not directly indicate excellent EM wave absorption capability. An ideal EM wave absorber must balance attenuation capability with optimal impedance matching to maximize EM wave penetration into the materials. Among the analyzed samples, HEB-Ti exhibited the best impedance matching alongside a moderate attenuation capability. Owing to the synergistic effect of these two factors, HEB-Ti thus exhibited superior EM wave absorption performance.

### 3.5 EM parameters and EM wave absorption mechanism

The EM wave absorption performance is strongly associated with the EM parameters. Therefore, the relative complex permeability ( $\mu_r = \mu' + j\mu''$ ) and relative complex permittivity ( $\epsilon_r = \epsilon' + j\epsilon''$ ) of the samples were analyzed in the frequency range of 2–18 GHz. According to the theory of EM wave energy conversion, the real parts of the permittivity ( $\epsilon'$ ) and permeability ( $\mu'$ ) are related to the ability of the absorbing materials to store EM energy, whereas the imaginary parts of the permittivity ( $\epsilon''$ ) and permeability ( $\mu''$ ) are related to the ability of the absorbing materials to dissipate EM energy [65]. As shown in Figs. 11(a) and 11(b), the  $\mu'$  and  $\mu''$

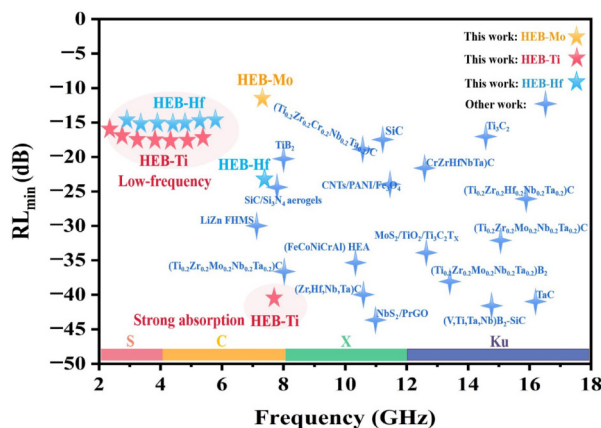


Fig. 9  $RL_{min}$  and optimal EAB of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) and some reported materials.

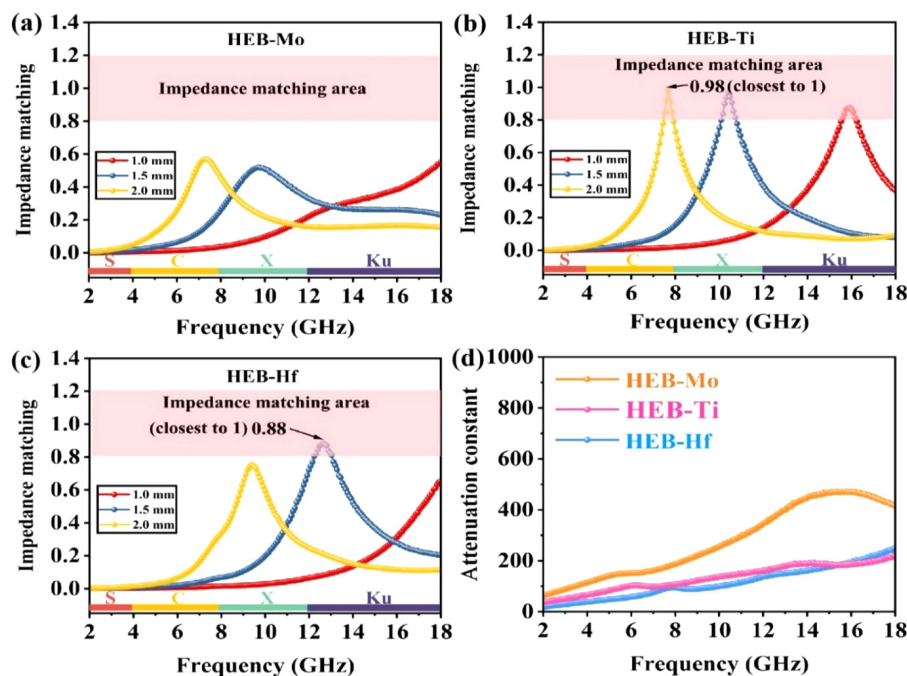


Fig. 10 (a–c) Impedance matching and (d) attenuation constant of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ).

values of all the samples were close to 1 and 0, respectively, indicating that the effect of high-entropy component regulation on the magnetic loss of the system was relatively small. The effect of high-entropy component regulation on the dielectric loss of the system was studied below.

As shown in Figs. 12(a) and 12(b), both the  $\epsilon'$  and  $\epsilon''$  values of all the samples decreased with increasing frequency, which may be related to dipole polarization and dispersion effects [66]. Additionally, the presence of multiple resonance peaks in the  $\epsilon'$  and  $\epsilon''$  curves can be noted, indicating a significant polarization-relaxation phenomenon in the materials [19,41]. By further comparison, HEB-Mo exhibited higher values of  $\epsilon'$  (36.15–16.05) and  $\epsilon''$  (17.87–8.90), indicating excellent EM wave energy storage and dissipation capabilities for EM waves. In contrast, the values of  $\epsilon'$  and  $\epsilon''$  for HEB-Ti slightly decreased, ranging from 31.26 to 24.09 and from 9.89 to 5.20, respectively, whereas HEB-Hf presented the lowest values of  $\epsilon'$  (20.11–16.02) and  $\epsilon''$  (5.36–3.58). Combined with the impedance matching analysis results (Figs. 10(a)–10(c)), HEB-Ti exhibited moderate  $\epsilon'$  and  $\epsilon''$  values, indicating good impedance matching between the materials and the external EM wave. To further evaluate the dielectric loss capability of HEB-Mo, HEB-Ti, and HEB-Hf, the dielectric loss tangent  $\tan\delta_e$  ( $\tan\delta_e = \epsilon''/\epsilon'$ ) was calculated and is presented in Fig. 12(c). The results indicated that the order of the dielectric loss capacity was HEB-Mo > HEB-Ti > HEB-Hf, which was consistent with the results of the attenuation constant (Fig. 10(d)).

To analyze the dielectric loss mechanism, Cole-Cole plots ( $\epsilon'' - \epsilon'$  curves) of HEB-Mo, HEB-Ti, and HEB-Hf were constructed, as shown in Fig. 13. The dielectric loss in materials is attributed to polarization relaxation and conduction loss, which can be categorized into interfacial and dipolar polarization [67]. The polarization relaxation can be delineated by Cole-Cole plots via Eqs. (7) and (8) [68]:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (2\pi f)^2 \tau^2} \quad (7)$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)2\pi f \tau}{1 + (2\pi f)^2 \tau^2} + \frac{\sigma}{2\pi f \epsilon_0} \quad (8)$$

By simplifying these equations, the relationship between  $\epsilon'$  and  $\epsilon''$  can be obtained as shown in Eq. (9) [69]:

$$\left(\epsilon' - \frac{\epsilon_s + \epsilon_\infty}{2}\right)^2 + (\epsilon'')^2 = \left(\frac{\epsilon_s - \epsilon_\infty}{2}\right)^2 \quad (9)$$

where  $\epsilon_s$  and  $\epsilon_\infty$  represent the static permittivity and permittivity at the high-frequency limit, respectively. Moreover,  $\tau$ ,  $\sigma$ , and  $\epsilon_0$  represent the polarization relaxation time, conductivity, and vacuum permittivity, respectively. Every occurrence of the Cole-Cole semicircle indicated the existence of one Debye relaxation process [70].

As shown in Figs. 13(a)–13(c), the Cole-Cole curves for all samples exhibited multiple regular circular processes, indicating the existence of multiple Debye relaxation mechanisms in EM fields, which were caused by dipole polarization. Notably, many irregular and distorted semicircles could be observed in HEB-Ti and HEB-Hf, indicating that other mechanisms, such as defect polarization, could also increase dielectric loss [71]. In addition, a slight linear tail could be observed at the end of all the Cole-Cole curves. This phenomenon indicated the existence of conduction loss. The linear tail slopes of different samples were different, reflecting their differences in electrical conductivity [72].

To further evaluate the contribution of conductivity loss, we evaluated the approximate electrical conductivities ( $\sigma_{AC}$ ) of the samples via free-electron theory and the measured  $\epsilon''$  values via the equation  $\sigma_{AC} = 2\pi\epsilon_0\epsilon''f$  [73], as illustrated in Fig. 13(d). The results revealed that the variation in sample conductivity was consistent with the characteristics of the end line of the Cole-Cole curve. Overall, HEB-Ti exhibited moderate  $H$  and  $\epsilon''$  values in the  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ) samples, enabling effective impedance matching and a balanced loss capacity. SEM, TEM, and EPR results indicated that HEB-Ti exhibited a moderate level of microstructural defects, including lattice

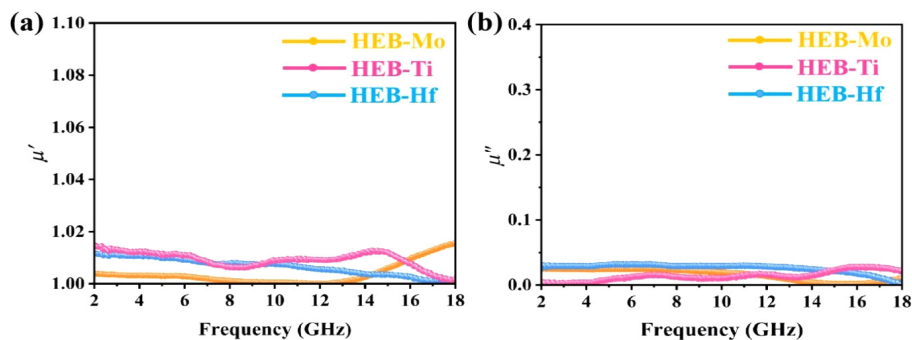


Fig. 11 (a) Real part and (b) imaginary part of complex permeability of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ).

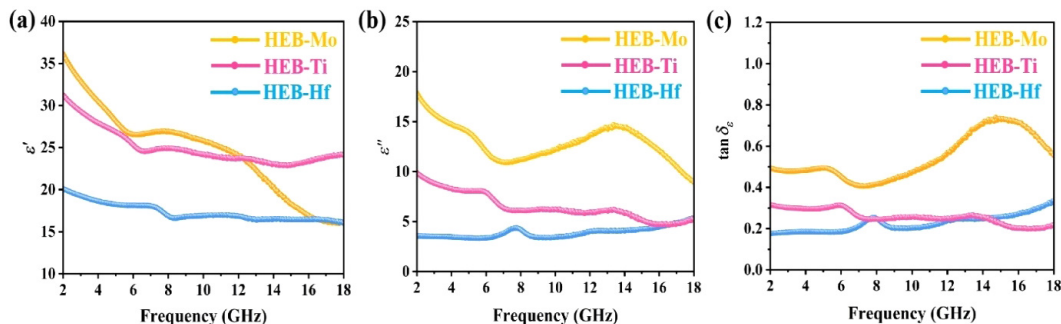


Fig. 12 (a) Real part and (b) imaginary part of complex permittivity and (c) the dielectric loss tangent of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ).

stacking, deformation, disappearance, and point defects. These defects induce multiple dielectric loss mechanisms, such as defect polarization, dipole polarization, and conduction loss. Under the synergistic influence of these mechanisms, HEB-Ti demonstrated exceptional absorbing properties.

As discussed above, HEB-Ti demonstrated superior EM wave absorption performance due to relatively moderate dielectric loss and good EM impedance matching. The EM wave absorption mechanisms of HEB-Ti are shown in Fig. 14. First, the presence of appropriate pores in HEB-Ti improved interface impedance matching, ensuring that more EM waves entered the materials and were absorbed rather than reflected. Second, since HEB-Ti has good electrical conductivity, free electrons in the system can absorb EM energy under EM wave radiation and increase the consumption of EM energy through electron migration within the material system [74]. Moreover, the formation of vacancy defects

in HEB-Ti led to the disruption of the original equilibrium states of polarization. Local charge separation and dipole formation under alternating electric fields increase the number of polarization loss sites. These defective sites generate many dipoles, which undergo dipole polarization in the presence of incident EM waves [75]. As a result, the EM wave absorption performance and impedance matching of HEB-Ti could be effectively improved.

## 4 Conclusions

In summary, three novel high-entropy materials ( $V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2}B_2$  ( $X = Mo, Ti, \text{ and } Hf$ )) were successfully synthesized within 10 min via a UHS apparatus at 1900 °C via Joule heating. In these material systems, compositional modulation significantly influences the microstructural characteristics of these materials. Notably, HEB-Ti exhibited an appropriate number of microstructural defects, including lattice

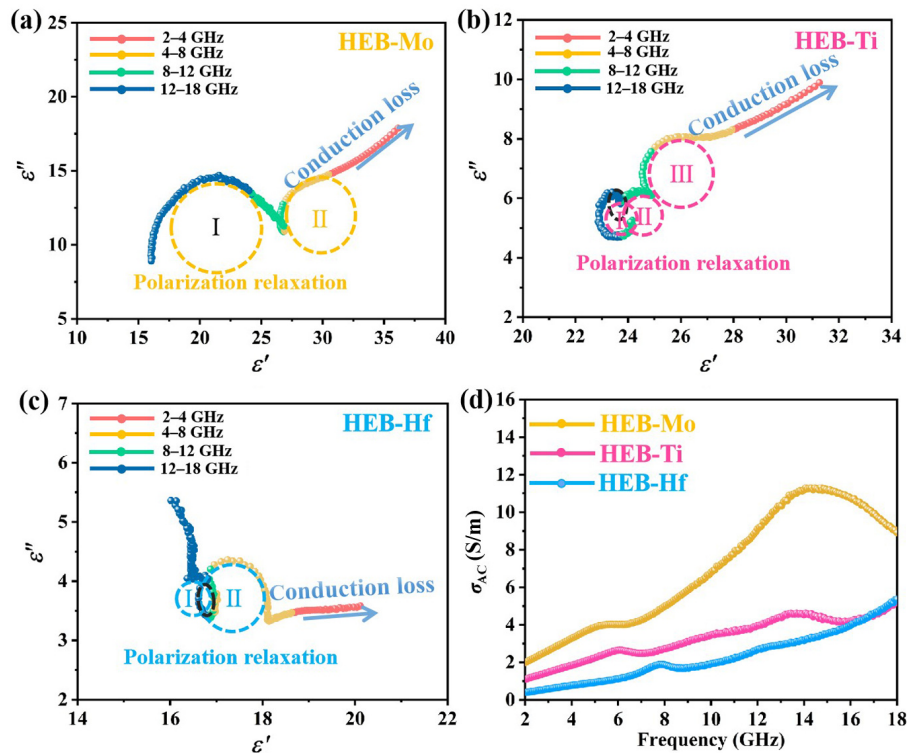


Fig. 13 (a-c) Cole-Cole curves and (d)  $\sigma_{AC}$  of  $(V_{0.2}Nb_{0.2}Zr_{0.2}Ta_{0.2}X_{0.2})B_2$  ( $X = Mo, Ti, \text{ and } Hf$ ).

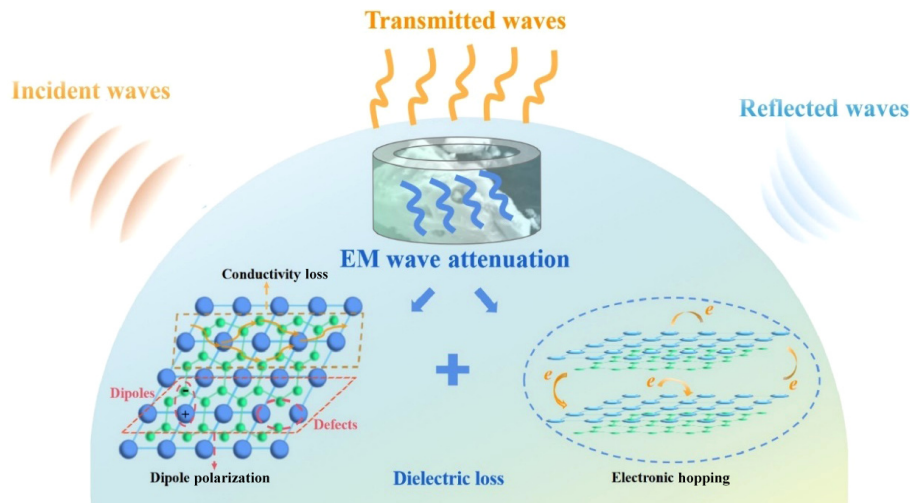


Fig. 14 Schematic illustration of mechanisms of EM wave absorption in HEB-Ti.

dislocations, stacking faults, and point defects. These defects trigger multiple dielectric loss mechanisms (defect polarization, dipole polarization, and conduction loss), thereby effectively absorbing EM waves. Moreover, the effect of high-entropy component on the magnetic loss of the system was relatively small, but the effect on the dielectric loss was larger. The HEB-Ti sample exhibited strong absorption properties due to relatively moderate dielectric loss and good EM impedance matching. Moreover, because of its relatively moderate attenuation constant, it could achieve the maximum penetration of the EM wave and the minimum reflection after absorbing wave. As a result, HEB-Ti demonstrated superior EM wave absorption performance. The maximum EAB covered the entire low-frequency range of 2–8 GHz, with a  $RL_{\min}$  of  $-40.7$  at 7.68 GHz and a thickness of 1.5 mm. In addition, HEB-Ti exhibited excellent thermal stability and can withstand temperatures up to 550 °C in air and 1000 °C in an argon gas environment. Owing to its excellent thermal stability and outstanding EM absorption performance, HEB-Ti ceramics are promising candidates for EM wave absorption in harsh environments.

### Acknowledgements

This work was supported by the National Key R&D Program of China (No. 2024YFB3816600), the Guangxi Natural Science Foundation (No. 2022GXNSFAA035527), the Natural Science Foundation of Tianjin (Nos. 23JCZDJC00150 and 22JCZDJC00080), the Science and Technology Major Project of Ningbo (No. 2021Z123), the Yongjiang Talent Introduction Programme (No. 2021A-108-G), the Youth Fund of the Chinese Academy of Sciences (No. JCPYJ-22030), and Guilin University of Technology Research Startup Fund (No. RD2100000621).

### Author contributions

Chencheng Liu is responsible for conceptualization, data curation, visualization, and writing—original draft. Qingyun Chen is responsible for conceptualization, funding acquisition, and writing—review & editing (Chencheng Liu and Qingyun Chen contributed equally to this work). Peng Sun is responsible for data curation. Xingye Wang is responsible for data curation, visualization, and writing—review & editing. Shuyi Zeng is responsible for formal analysis. Qijie Chen is responsible for data curation. Tong Zhu is responsible for formal analysis and investigation. Yi Zhu is responsible for data curation. Wenlong Zhang is responsible for data curation. Hui Song is responsible for formal analysis. Yuezong Wang is responsible for funding acquisition, investigation, and writing—review & editing. Kazuhito Nishimura is responsible for conceptualization and funding acquisition. Huasong Liu is responsible for investigation and writing—review & editing. Nan Jiang is responsible for conceptualization and funding acquisition.

### Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

### Data availability statement

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

### References

- [1] Zhang W, Su L, Lu D, *et al.* Resilient  $\text{Si}_3\text{N}_4/\text{SiO}_2$  nanowire aerogels for high-temperature electromagnetic wave transparency and thermal insulation. *J Adv Ceram* 2023, **12**: 2112–2122.
- [2] Wang L, Cai ZX, Su L, *et al.* Bifunctional  $\text{SiC}/\text{Si}_3\text{N}_4$  aerogel for highly efficient electromagnetic wave absorption and thermal insulation. *J Adv Ceram* 2023, **12**: 309–320.
- [3] Xia QS, Han Z, Zhang ZC, *et al.* High temperature microwave absorbing materials. *J Mater Chem C* 2023, **11**: 4552–4569.
- [4] Ma JB, Zhao B, Xiang HM, *et al.* High-entropy spinel ferrites  $\text{MFe}_2\text{O}_4$  ( $\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) with tunable electromagnetic properties and strong microwave absorption. *J Adv Ceram* 2022, **11**: 754–768.
- [5] Wu T, Liu Y, Zeng X, *et al.* Facile hydrothermal synthesis of  $\text{Fe}_3\text{O}_4/\text{C}$  core-shell nanorings for efficient low-frequency microwave absorption. *ACS Appl Mater Inter* 2016, **8**: 7370–7380.
- [6] Kim T, Lee J, Lee K, *et al.* Magnetic and dispersible  $\text{FeCoNi}$ -graphene film produced without heat treatment for electromagnetic wave absorption. *Chem Eng J* 2019, **361**: 1182–1189.
- [7] Che RC, Peng LM, Duan XF, *et al.* Microwave absorption enhancement and complex permittivity and permeability of Fe encapsulated within carbon nanotubes. *Adv Mater* 2004, **16**: 401–405.
- [8] Cao YC, Ye F, Liang J, *et al.* Structural-functional-integrated ultra-wideband microwave-absorbing composites based on *in situ*-grown graphene meta-nanointerface. *Adv Funct Mater* 2024, **34**: 2411271.
- [9] Yu ZJ, Chen T, Du HZ, *et al.* Single-source-precursor derived SiOC ceramics with *insitu* formed CNTs and core-shell structured  $\text{CoSi@C}$  nanoparticles towards excellent electromagnetic wave absorption properties. *J Adv Ceram* 2023, **12**: 1119–1135.
- [10] Yin XM, Li HJ, Yuan RM, *et al.* Metal-organic framework derived hierarchical  $\text{NiCo}_2\text{O}_4$  triangle nanosheet arrays@SiC nanowires network/carbon cloth for flexible hybrid supercapacitors. *J Mater Sci Technol* 2021, **81**: 162–174.
- [11] Zhang XL, Li WW, Wan S, *et al.* Pressure dependence of the electrical conductivities of high-entropy diborides. *J Eur Ceram Soc* 2022, **42**: 6951–6957.
- [12] Wen ZH, Meng H, Jiang SD, *et al.* Non-equimolar  $(\text{Hf}, \text{Zr}, \text{Ta}, \text{W})\text{B}_2$  high-entropy diborides enable superior oxidation resistance. *Sci China Mater* 2023, **66**: 3213–3222.
- [13] Qi W, Chen B, Yang X, *et al.* Phase stability, mechanical and thermodynamic properties of  $(\text{Hf}, \text{Zr}, \text{Ta}, \text{M})\text{B}_2$  ( $\text{M} = \text{Nb}, \text{Ti}, \text{Cr}, \text{W}$ ) quaternary high-entropy diboride ceramics via first-principles calculations. *Ceram Int* 2023, **49**: 33255–33264.
- [14] Gao W, Wang XG, Wang XF, *et al.* Preparation of  $(\text{Ti}, \text{Zr}, \text{Hf})\text{B}_2$  powders and effect of  $\text{B}_4\text{C}$  content on the high temperature flexural strength of medium entropy ceramics. *Advanced Ceramics* 2023, **44**: 342–351. (in Chinese)
- [15] Tallarita G, Licheri R, Garroni S, *et al.* High-entropy transition metal diborides by reactive and non-reactive spark plasma sintering: A comparative investigation. *J Eur Ceram Soc* 2020, **40**: 942–952.
- [16] Guo RR, Li ZJ, Li L, *et al.* Microstructures and oxidation mechanisms of  $(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2})\text{B}_2$  high-entropy ceramic. *J Eur Ceram Soc* 2022, **42**: 2127–2134.
- [17] Qiao LJ, Bi JQ, Liang GD, *et al.* Synthesis and electromagnetic wave absorption performances of a novel  $(\text{Mo}_{0.25}\text{Cr}_{0.25}\text{Ti}_{0.25}\text{V}_{0.25})_3\text{AlC}_2$  high-entropy MAX phase. *J Mater Sci Technol* 2023, **137**: 112–122.
- [18] Wang HH, Xiao XY, Zhai SR, *et al.* Spontaneous orientation polarization of anisotropic equivalent dipoles harnessed by entropy engineering for ultra-thin electromagnetic wave absorber. *Nano-Micro Lett* 2025, **17**: 19.
- [19] Cheng JY, Li Y, Raza H, *et al.* Cross-scale synergistic manipulation of dielectric genes in polycrystalline sulfides from micropolarization to macroconductance toward wide-band microwave absorption. *Adv Funct Mater* 2024: 2405643.
- [20] Zhang WM, Dai FZ, Xiang HM, *et al.* Enabling highly efficient and broadband electromagnetic wave absorption by tuning impedance match in high-entropy transition metal diborides ( $\text{HE TM}_2\text{B}_2$ ). *J Adv Ceram* 2021, **10**: 1299–1316.
- [21] Chen H, Xiang HM, Dai FZ, *et al.* Porous high entropy  $(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{B}_2$ : A novel strategy towards making ultrahigh temperature ceramics thermal insulating. *J Mater Sci Technol* 2019, **35**: 2404–2408.

- [22] Gild J, Kaufmann K, Vecchio K, *et al.* Reactive flash spark plasma sintering of high-entropy ultrahigh temperature ceramics. *Scripta Mater* 2019, **170**: 106–110.
- [23] Liu D, Wen TQ, Ye BL, *et al.* Synthesis of superfine high-entropy metal diboride powders. *Scripta Mater* 2019, **167**: 110–114.
- [24] Shen XQ, Liu JX, Li F, *et al.* Preparation and characterization of diboride-based high entropy  $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{B}_2$ -SiC particulate composites. *Ceram Int* 2019, **45**: 24508–24514.
- [25] Feng L, Fahrenholtz WG, Hilmas GE. Processing of dense high-entropy boride ceramics. *J Eur Ceram Soc* 2020, **40**: 3815–3823.
- [26] Feng L, Monteverde F, Fahrenholtz WG, *et al.* Superhard high-entropy  $\text{AlB}_2$ -type diboride ceramics. *Scripta Mater* 2021, **199**: 113855.
- [27] Feltrin AC, Hedman D, Akhtar F. Transformation of metastable dual-phase  $(\text{Ti}_{0.25}\text{V}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25})\text{B}_2$  to stable high-entropy single-phase boride by thermal annealing. *Appl Phys Lett* 2021, **119**: 161905.
- [28] Wang CW, Ping WW, Bai Q, *et al.* A general method to synthesize and sinter bulk ceramics in seconds. *Science* 2020, **368**: 521–526.
- [29] Guo M, Dong Q, Xie H, *et al.* Ultrafast high-temperature sintering to avoid metal loss toward high-performance and scalable cermets. *Matter* 2022, **5**: 594–604.
- [30] Deng B, Wang Z, Choi CH, *et al.* Kinetically controlled synthesis of metallic glass nanoparticles with expanded composition space. *Adv Mater* 2024, **36**: 2309956.
- [31] Tallarita G, Licheri R, Garroni S, *et al.* Novel processing route for the fabrication of bulk high-entropy metal diborides. *Scripta Mater* 2019, **158**: 100–104.
- [32] Ban QF, Li LW, Li Y, *et al.* Polymer self-assembly guided heterogeneous structure engineering towards high-performance low-frequency electromagnetic wave absorption. *J Colloid Interf Sci* 2023, **650**: 1434–1445.
- [33] Zhu T, Wu H, Zhou R, *et al.* Microstructures and tribological properties of TiC reinforced FeCoNiCuAl high-entropy alloy at normal and elevated temperature. *Metals* 2020, **10**: 387.
- [34] Hine R. Elementary derivation of the Bragg equation. *Am J Phys* 1965, **33**: 962–963.
- [35] Yang Y, Bi JQ, Sun KN, *et al.* The effect of chemical element on hardness in high-entropy transition metal diboride ceramics. *J Eur Ceram Soc* 2023, **43**: 5774–5781.
- [36] Wang YC, Csanádi T, Zhang HF, *et al.* Synthesis, microstructure, and mechanical properties of novel high entropy carbonitrides. *Acta Mater* 2022, **231**: 117887.
- [37] Yang TT, Li Y, Wu WW, *et al.* The synergistic effect of dual substitution of Al and Sb on structure and ionic conductivity of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  ceramic. *Ceram Int* 2018, **44**: 1538–1544.
- [38] Zhang HH, Liu H, Wu HB, *et al.* Microwave absorbing property of gelcasting SiC-Si<sub>3</sub>N<sub>4</sub> ceramics with hierarchical pore structures. *J Eur Ceram Soc* 2022, **42**: 1249–1257.
- [39] Feng ZB, Liu CB, Li X, *et al.* Designing electronic structures of multiscale helical converters for tailored ultrabroad electromagnetic absorption. *Nano-Micro Lett* 2024, **17**: 20.
- [40] Li FS, Wu NN, Kimura H, *et al.* Initiating binary metal oxides microcubes electromagnetic wave absorber toward ultrabroad absorption bandwidth through interfacial and defects modulation. *Nano-Micro Lett* 2023, **15**: 220.
- [41] Hu RZ, He X, Luo YQ, *et al.* Biomimetic multi-interface design of raspberry-like absorbent: Gd-doped  $\text{FeNi}_3$ @covalent organic framework derivatives for efficient electromagnetic attenuation. *Small Methods* 2024: 2401299.
- [42] Feltrin AC, Akhtar F. High-temperature oxidation kinetics of a metastable dual-phase diboride and a high-entropy diboride. *J Eur Ceram Soc* 2023, **43**: 7363–7372.
- [43] Tang ZY, Wen ZH, Liu YW, *et al.* Rapid experimental screening of high-entropy diborides for superior oxidation resistance. *Adv Funct Mater* 2024, **34**: 2312239.
- [44] Zhang WM, Zhao B, Xiang HM, *et al.* One-step synthesis and electromagnetic absorption properties of high entropy rare earth hexaborides (HE REB<sub>6</sub>) and high entropy rare earth hexaborides/borates (HE REB<sub>6</sub>/HE REBO<sub>3</sub>) composite powders. *J Adv Ceram* 2021, **10**: 62–77.
- [45] Green M, Liu Z, Xiang P, *et al.* Ferric metal-organic framework for microwave absorption. *Mater Today Chem* 2018, **9**: 140–148.
- [46] Wen HL, Xu W, Lin S, *et al.* Enhanced microwave absorption using multiple heterostructures derived from *in situ* grown Sn-metal-organic framework on La-doped Fe<sub>3</sub>O<sub>4</sub>. *Carbon* 2024, **230**: 119613.
- [47] Lin S, Lin J, Xiong ZQ, *et al.* Micro-helical Ni<sub>3</sub>Fe chain encapsulated in ultralight MXene/C aerogel to realize multi-functionality: Radar stealth, thermal insulation, fire resistance, and mechanical properties. *Chem Eng J* 2024, **492**: 152248.
- [48] Fan BB, Shang SY, Dai BZ, *et al.* 2D-layered Ti<sub>3</sub>C<sub>2</sub>/TiO<sub>2</sub> hybrids derived from Ti<sub>3</sub>C<sub>2</sub> MXenes for enhanced electromagnetic wave absorption. *Ceram Int* 2020, **46**: 17085–17092.
- [49] Jian X, Tian W, Li JY, *et al.* High-temperature oxidation-resistant ZrN<sub>0.4</sub>B<sub>0.6</sub>/SiC nanohybrid for enhanced microwave absorption. *ACS Appl Mater Inter* 2019, **11**: 15869–15880.
- [50] Song ZR, Sun MX, Wu LP, *et al.* Dielectric loss behavior and microwaves absorption properties of TiB<sub>2</sub> ceramic. *Mater Res Express* 2020, **7**: 046301.
- [51] Zhou YC, Zhao B, Chen H, *et al.* Electromagnetic wave absorbing properties of TMCs (TM = Ti, Zr, Hf, Nb and Ta) and high entropy  $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{C}$ . *J Mater Sci Technol* 2021, **74**: 105–118.
- [52] Wu RB, Zhou K, Yang ZH, *et al.* Molten-salt-mediated synthesis of SiC nanowires for microwave absorption applications. *Cryst Eng Comm* 2013, **15**: 570–576.
- [53] Qing YC, Zhou WC, Luo F, *et al.* Titanium carbide (MXene) nanosheets as promising microwave absorbers. *Ceram Int* 2016, **42**: 16412–16416.
- [54] Wang WL, Sun GX, Sun XN, *et al.* Electromagnetic wave absorbing properties of high-entropy transition metal carbides powders. *Mater Res Bull* 2023, **163**: 112212.
- [55] Zhang WM, Xiang HM, Dai FZ, *et al.* Achieving ultra-broadband electromagnetic wave absorption in high-entropy transition metal carbides (HE TMCs). *J Adv Ceram* 2022, **11**: 545–555.
- [56] Yang PP, Liu Y, Zhao XC, *et al.* Electromagnetic wave absorption properties of mechanically alloyed FeCoNiCrAl high entropy alloy powders. *Adv Powder Technol* 2016, **27**: 1128–1133.
- [57] Cai XD, Guo HQ, Zhu HJ, *et al.* Effect of cooling medium on the preparation and microwave absorption properties in low frequency for LiZn ferrites hollow microspheres. *J Alloys Compd* 2022, **906**: 164290.
- [58] Liu CC, Chen QY, Li XH, *et al.* Low-temperature synthesis of a novel diboride ceramic with electromagnetic wave absorption properties. *J Mater Sci-Mater El* 2024, **35**: 287.
- [59] Gong YB, Yang ZG, Wei XG, *et al.* Synthesis and electromagnetic wave absorbing properties of high-entropy metal diboride-silicon carbide composite powders. *J Mater Sci* 2022, **57**: 9218–9230.
- [60] Dai D, Lan XL, Wu LN, *et al.* Designed fabrication of lightweight SiC/Si<sub>3</sub>N<sub>4</sub> aerogels for enhanced electromagnetic wave absorption and thermal insulation. *J Alloys Compd* 2022, **901**: 163651.
- [61] Du H, Zhang QP, Zhao B, *et al.* Novel hierarchical structure of MoS<sub>2</sub>/TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> composites for dramatically enhanced electromagnetic absorbing properties. *J Adv Ceram* 2021, **10**: 1042–1051.
- [62] Li Y, Jin YH, Cheng JY, *et al.* Achieving superior electromagnetic wave absorbers with 2D/3D heterogeneous structures through the confinement effect of reduced graphene oxides. *Carbon* 2023, **213**: 118245.
- [63] Peng HL, Xiong ZQ, Gan ZH, *et al.* Microcapsule MOFs@MOFs derived porous “nut-bread” composites with broadband microwave absorption. *Compos Part B-Eng* 2021, **224**: 109170.
- [64] Gao Y, Du H, Li RR, *et al.* Multi-phase heterostructures of flower-like Ni(NiO) decorated on two-dimensional Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/TiO<sub>2</sub> for high-performance microwave absorption properties. *Ceram Int* 2021, **47**: 10764–10772.
- [65] Wang JW, Sun QH, Li JY, *et al.* Polymer-based nanocomposites: Role of interface for effective microwave absorption. *Mater Today Phys* 2023, **31**: 100981.

- [66] Xu BK, He QC, Wang YQ, *et al.* Ultralight and efficient microwave absorption of SiC/SiO<sub>2</sub> ceramic aerogels derived from biomass. *Ceram Int* 2023, **49**: 30125–30136.
- [67] Tian YX, Huang M, Kong NZ, *et al.* Designing insulative SiC coating layer on the artificial graphite particle to achieve synergy of wave absorption and thermal conduction. *Carbon* 2023, **214**: 118352.
- [68] Liu C, Qiao J, Zhang X, *et al.* Noncovalent self-assembly of a minuscule amount of nickel porphyrin on carbon nanotube for high-performance electromagnetic wave absorbing. *Compos Part A-Appl S* 2023, **164**: 107281.
- [69] Zhao B, Shao G, Fan BB, *et al.* Facile synthesis and novel microwave electromagnetic properties of flower-like Ni structures by a solvothermal method. *J Mater Sci-Mater El* 2014, **25**: 3614–3621.
- [70] Liu CC, Zhu T, Jia J, *et al.* Facile synthesis of novel nitrogen-doped diamond with excellent microwave absorption and thermal conductive performance. *Diam Relat Mater* 2025, **151**: 111789.
- [71] Liu P, Ng VMH, Yao Z, *et al.* Facile synthesis and hierarchical assembly of flowerlike NiO structures with enhanced dielectric and microwave absorption properties. *ACS Appl Mater Inter* 2017, **9**: 16404–16416.
- [72] Fu YR, Wang YP, Cheng JY, *et al.* Manipulating polarization attenuation in NbS<sub>2</sub>-NiS<sub>2</sub> nanoflowers through homogeneous heterophase interface engineering toward microwave absorption with shifted frequency bands. *Nano Mater Sci* 2024, **6**: 794–804.
- [73] Guan GG, Yan L, Zhou YT, *et al.* Composition design and performance regulation of three-dimensional interconnected FeNi@carbon nanofibers as ultra-lightweight and high efficiency electromagnetic wave absorbers. *Carbon* 2022, **197**: 494–507.
- [74] Wang J, Wang YP, Cheng JY, *et al.* Abundant vacancies induced high polarization-attenuation effects in flower-like WS<sub>2</sub> microwave absorbers. *J Mater Sci Technol* 2024, **194**: 193–202.
- [75] Zhao HQ, Cheng Y, Zhang Z, *et al.* Biomass-derived graphene-like porous carbon nanosheets towards ultralight microwave absorption and excellent thermal infrared properties. *Carbon* 2021, **173**: 501–511.